AN INVESTIGATION INTO MEASURING AMMONIA LOSS DURING THE OPERATION OF A FREESTALL DAIRY BARN

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Abstract

The dairy sector in New Zealand (NZ) has undergone rapid intensification and transformation over the past few decades: the traditional pasture based grazing systems are continuously being replaced by high supplement feed input system like feed pads, herd homes and wintering barns. Practising duration controlled grazing; using temporary housing systems (naturally ventilated barns) can reduce urinary load to paddocks and N loss to water. There is concern that ammonia (NH_3) loss to the atmosphere during housing, manure storage and re-application to pasture simply results in pollution swapping i.e. decreasing N loss to water while increasing the greenhouse gas emission footprint of dairying.

The main objective of this research was to develop cost effective techniques to monitor, mitigate and minimise the NH_3 gas emissions from a duration controlled grazing system in the Manawatu region of NZ. The main components of dairy cattle (DC) grazing systems are feed, housing, storage and slurry reapplication to land. The first study focused on developing techniques to identify the hotspots contributing to gas emissions from all stages of the manure management chain. The efficiency of two commonly used techniques namely active and passive NH_3 gas sampling was evaluated and modified. Commonly used 7 L dynamic chambers and large vacuum pumps were replaced by small 50 ml PVC tube acid scrubbers and small aquarium pumps. The acid scrubbers were successfully deployed for NH_3 gas emission measurements from storage pond and slurry re-application to land. Simple diffusion sampling tubes (DSTs) were also developed and calibrated for long term measurements from storage ponds.

The second set of laboratory experiments aimed at studying the losses associated with the feed component. The effect of diet on urine N content excreted by dairy cows and the influence of urea N content of urine on the magnitude of NH_3 emissions was studied by simulating excreta deposition on a barn floor in 1 L Agee jars. In NZ dairy cows are fed on pasture based production system, however when the pasture becomes limiting during summers then cows are fed on high supplement feed inputs like maize and hay silage. It was hypothesised that dietary manipulation would impact N excretion and NH_3 emissions from excreta. For this experiment, a total of fifty four dairy cows were used. They were

split into three groups (each group containing 18 cows) and fed on high crude protein (HCP, 25%), medium crude proteins (MCP, 18.5%) and low crude proteins (LCP, 13.5%) diets. Urine and dung samples were collected separately from each group of the cows. NH_3 emissions from the slurry mixture were measured in vitro in a laboratory set up at room temperature (18 ºC - 24 ºC) for 6 days. The laboratory set up consisted of 11 Agee jars (1 L) with passive acid traps (10 ml 0.5 M H_2SO_4) contained in 50 ml pink tops. The slurry mixture was reconstituted at a standard rate of excretion by dairy cows at a ratio of 1 : 1.3 (dung: urine) by mixing the freshly collected urine and dung [(w/v); wet basis] in urine containers. The cumulative NH_3 losses were reported based on the urea N applied and total Kjeldahl N applied to each Agee jar. The results showed that NH_3 emissions reduced by 13 - 20% with decrease in dietary crude protein. It was concluded that manipulating the CP level in diet can reduce urinary N excretion from dairy cows and hence lower NH_3 emissions.

A subsequent series of laboratory experiments were conducted using 1 L Agee jars to quantify NH_3 losses from various hotspots in a naturally ventilated dairy cow barn to study the factors affecting NH_3 emissions. The main sources of NH_3 losses from the barn are excreta deposited on laneways, scraper lanes and slurry collection pits located underneath the barn. In Study 1, aged slurry samples were taken from different positions in the slurry pathway from channel grate to the storage pond. In Experiment 2 of study 1 (Ex-situ measurements), sources of fresh slurry were created (by mixing urine and dung) to represent the different depths of fresh slurry deposited in the free-stall barn's laneways and under the grates in the transport channel. The NH_3 emission rate from all slurry samples were measured in closed chambers. In study 2 (In situ measurements), a 3D sonic anemometer and NH_3 acid traps were used to measure airflow rates and NH_3 concentrations in the barns ventilation pathways. The barn's estimated NH_3 emissions calculated from the two contrasting studies were compared.

There is limited NZ data on NH_3 gas emissions from a slurry storage pond receiving slurry from a wintering barn. NH_3 gas emissions were monitored in the winter of 2017 (2nd June to 16th August) by modified integrated horizontal flux (IHF) methodology. The gas emission flux was measured using diffusion sampling tubes (DSTs) placed at sampling heights (0.25 m to 3.5 m) on an aluminium tower. The towers were mounted at 4 banks (N, S, E, W) of the pond and DSTs were changed every 72 or 94 h. The gas emission flux

was found to be positively correlated to daily evapotranspiration rate (ETR) (R^2=0.80) and this relationship was used to predict gaseous emission from a static pond.

The slurry is usually stored up-to 3 months before re-application to land. NH_3 gas emission from the final stage of manure management was measured on two occasions; Summer 2015 and Autumn 2016. Slurry was incorporated in land through slurry surface spray and injection and losses were measured using IHF methodology. Slurry was applied at 81 kg N ha^{-1} for surface spray and 73 kg N ha^{-1} was injected into the soil through injection. Similarly the application rate for autumn application was 252 kg N ha^{-1} for surface spray and 233 kg N ha^{-1} for injection application. The percentage NH_3-N losses were 2% from slurry surface spray and 1.4% from slurry incorporation through injection for summer application and 3% from slurry surface spray and only 1% from injected application of slurry in autumn.

On completion of NH_3 loss measurements at all stages of manure management it was possible to construct a partial NH_3 loss budget to illustrate the relative NH_3 losses associated with the temporary housing of cows in a freestall barn, manure storage and reapplication to land. This simple analysis illustrated that the largest loss of NH_3 can occur if there is a long storage phase of effluent in a open pond. Future research to mitigate NH_3 losses created by housing cows should focus on the reduction of NH_3 loss from ponds.

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This work is dedicated to "myself" and to "all who had given me dreams to look forward to"

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Chapter 1

Introduction

1.1 Issue

Agricultural intensification and fertilizer use led to two-fold increases in ammonia (NH_3) emissions globally since the pre-industrial times (Clarisse et al. 2009). Livestock farming has been identified as the major source of NH_3 emissions which cause many environmental issues. The escape of NH_3 into the atmosphere reduces the air quality thereby accelerating the formation of particulate matter, and when deposited in water and land may cause acidification and the nutrient N-enrichment of natural ecosystems (Erisman et al. 2008). Globally agricultural practices contribute 94% of anthropogenic NH_3 emissions of which 64% associated with livestock farming practices (Steinfeld et al. 2006). Within livestock production systems, dairy farming is the largest source of NH_3 emissions (Steinfeld et al. 2006). The most important sources of NH_3 emissions are intensive dairy farming practices (grazed and housed), animals and manure It is important that each country that is a signatory to Kyoto Protocol is able to measure, monitor and reduce its NH_3 emissions to its greenhouse gas (GHG) inventory if global warming is to be mitigated. New Zealand being a Kyoto Protocol signatory is compelled to minimize its GHG emissions to 1990 levels.

The agricultural sector is th economic powerhouse of New Zealand (NZ) generating 60% of export revenue. Unfortunately agricultural activities are also the main contributor of GHG and leaching losses of N to the environment. About 48.1% of NZ's GHG emissions originate from agricultural activities (Ministry for the Environment 2019). New Zealand leads in global dairy production and the dairy sector contributed 21% to total country's export http://www.environmentguide.org.nz/agriculture/. Favourable weather conditions for pasture and fodder growth in NZ and high demand for NZ dairy products has led to increase in dairy cattle population and increased use of nitrogen (N) containing fertilisers to enhance pasture production. This intensification causes atmospheric pollution through gaseous emission of N such as ammonia (NH_3) and nitrous oxide (N_2O) and N losses to waterways such as nitrate (NO_3^-) leaching. NH_3 emissions represent

economic losses of N fertiliser and can cause eutrophication and acidification of water and soils, which have negative impacts on the flora and fauna, and biodiversity of NZ ecosystems. Indications are that in some intensive dairy farming areas of NZ atmospheric inputs for adjacent native ecosystems are above the critical 5 kg N ha^{-1} yr^{-1} limit established by (Ministry for the Environment 2000). Using a NZ specific 10% emission factor for ammonia emission (Sherlock, Jewell, and Clough 2008), Saggar et al. (2013) estimated that NZ livestock farming annually emits 130,000 tonnes of ammonia-N from animal deposition of urine, applied fertilisers and farm dairy effluent. This dispersed loss of NH_3-N has a value of $164 m/year based on $580/t urea.

NZ dairy farming has traditionally been pasture based but over the past few decades it has underdone rapid changes and intensification with the introduction of standoff facilities and barns to assist with the management of winter wet soils (Howes, Horne, and Shadbolt 2014), reduce N loss from drainage events (Christensen et al. 2019) and allow herd expansion without increasing the area of grazed pasture. Whereas GHG and NH_3 emissions from excreta deposition on dairy grazed pastures in NZ has been extensively measured and reviewed (Saggar et al. 2004; Luo et al. 2004; Luo and Saggar 2008; Sherlock et al. 2008; Laubach et al. 2013, 2015; Selbie, Buckthought, and Shepherd 2015), there is a dearth of quantitative data on NH_3 losses during the operation of a stand-off facilities and barns. Unlike fully housed systems in the US and EU, in NZ partial standoff or housing of cows occur to suit wet soil conditions and or supplement feeding to cows. It is not known how various factors (manure chemical characteristics and environmental) and management practices are going to influence the release of NH_3 gas from various stages of manure management. These stages are (i) supplementary feeding (ii) excreta deposited on house floor (iii) manure storage and (iv) application of stored manure to land. It is important to study the factors promoting NH_3 emissions from all the stages to develop emission factors and to mitigate these losses.

The availability of suitable and inexpensive techniques is very important to quantify gas emissions. The magnitude of emissions and factors influencing emissions from dietary intake, excreta deposition on barn floors, scraping schedules, emissions from fresh and aged slurry in storage pits, durations of storage and techniques of manure re-application can only be studied if proper measurement techniques are available. Secondly, it is very

important to know what stage of dairy farm operations is contributing most to NH_3 volatilization losses.

1.2 Research Objectives and Thesis Structure

Therefore the objectives of this research work were to develop efficient and inexpensive techniques (Chapter 3) suitable for measuring NH_3 losses and then to use these methods to study the influence of cow's diet (Chapters 4 and 5) and urine and dung characteristics and from all the four main stages (Chapters 6, 7 and 8) of freestall barn operation on NH_3 emissions. In summary, (Chapter 9) a simple case study illustrates which of the stages of freestall barn operation contributes most to NH_3 volatilization losses. Further research is recommended to confirm the extent of these losses and the suggested mitigation strategies to reduce them.

List of publications:

Conference proceedings

Malik K, Bishop PA, Saggar S, Hedley MJ (2016) [Abstract & Poster] Development of protocols for quantifying Ammonia volatilization losses from subsequent stages of manure management. 'In: Integrated nutrient and water management for sustainable farming'. (Eds LD Currie, R Singh). Occasional Report No. 29. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand. http://flrc.massey.ac.nz/publications.html. Occasional Report No. 29. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand. 9-11 February 2016.

Malik K, Bishop PA, Saggar S, Hedley MJ (2017) [Abstract & Poster] A longitudinal study to estimate NH_3-N losses associated with temporary housing of dairy cows and manure management. In: Science and policy: nutrient management challenges for the next generation. http://flrc.massey.ac.nz/publications.html. Occasional Report No. 30. Fertilizer and Lime Research Centre, Massey University, Palmerston North, New Zealand. 7-9 February 2017.

Conference abstracts

Malik K, Bishop PA, Saggar S, Hedley MJ (2016) [Abstract] Development of protocols for quantifying Ammonia volatilization losses from subsequent stages of manure management. 'In: Annual NzONet, MethaNet and CarboNet meeting', Wellington, New Zealand.

Malik K, Bishop PA, Saggar S, Hedley MJ (2016) [Abstract] Components of Nitrogen Loss from a Hybrid Dairy Grazing/Housing System 'In: Soil, a balancing act downunder'. Joint Conference for the New Zealand Society of Soil Science and Soil Science Australia, Queenstown, New Zealand.

Malik K, Bishop PA, Saggar S, Hedley MJ (2017) [Abstract] Nitrogen losses from the subsequent stages of manure management. 'In: Annual NzONet, MethaNet and CarboNet meeting'. Wellington, New Zealand.

Malik K, Bishop PA, Saggar S, Hedley MJ (2017) [Abstract] Nitrogen losses from the subsequent stages of manure management. 'In: Visions for the future'. Institute of Agriculture and Environment Symposium, Massey University, Palmerston North, New Zealand.

Malik K, Kyamanywa N, Bishop PA, Saggar S, Hedley MJ (2018) [Abstract] The influence of manipulating dietary crude protein intake on partially housed dairy cows on Nitrogen excretion and Ammonia emissions. 'In: Diverse soils - Productive landscapes. New Zealand Society of Soil Science Conference, Napier, New Zealand.

Chapter 2

Review of literature

2.1 Background

The dairy sector of New Zealand (NZ) is the powerhouse of the country's economy contributing $7.8 billion (3.5%) to total GDP. Dairy farming alone contributes $5.96 billion while remaining $1.88 billion is contributed by dairy processing. Nationally, dairy cattle population has increased from 3.8 million to 6.5 million (by 70%) since 1994. (https://www.stats.govt.nz/livestock-numbers). In NZ, a very small number of dairy farmers (no more than 3%) were using housing (Luo et al. 2013) but with the expansion in dairying and increasing land value this number has been increasing slowly in the last 7 years. Housing dairy cows could become a significant source of NH_3 emission causing detrimental effects to the environment. Ammonia loss from dairy operations is an instantaneous process which begins soon after excretion and mixing of urine and dung, and continues during manure handling, storage and land application of manure. The key factors driving NH_3 emission from housed dairy cow excreta are; stocking rate, diet, housing structure, flooring type, type of ventilation, relative humidity, temperature and the pH of the manure. In some overseas studies NH_3 gas emissions from dairy cattle barns are reported to be 20% to 55% of total N excreted as manure (Powell, Broderick, and Misselbrook 2008; Velthof et al. 2012). While NH_3 emissions from overseas confined dairy operations have been extensively reviewed (Ndegwa et al. 2008; Hristov et al. 2011; Laubach et al. 2015; Owen and Silver, 2015) and reported there is no quantitative information on NH_3 losses from hybrid dairy systems that involve grazing pasture combined with periodic housing. It is also not known how the NH_3 emissions will vary with the method of manure storage and storage conditions, and subsequent application of manure to pasture land. In NZ, NH_3 losses from animal housing should be included in the determination of the impact of wintering barns and use of free-stall barns in duration-controlled grazing systems on total NH_3 losses. Therefore quantitative NZ data on NH_3 emissions from confined barn systems from slurries and solid manures are needed to provide precise NH_3 emissions data for animal housing system and also to devise strategies and tools to mitigate these losses.

This review briefly describes the NZ dairy farming systems and off-grazing facilities, brings together fundamental aspects of the processes and the factors regulating NH_3 emission from animal excreta deposited in ventilated animal housing systems and describes the available methods for measuring NH_3 emissions in the barn systems from stored slurries and manures. The penultimate section focuses on quantifying NH_3 emission in NZ barn systems in general and from the Massey University free-stall barn system in particular.

Traditional grass based dairy systems (System 1) are being replaced by more intensive systems which require a greater amount of supplementary feed input. According to DairyNZ (Livestock Improvement Corporation and DairyNZ 2013) the number of System 1 (pastures based) farms has been reduced from 41% to 10% whereas the number of System 2 farms (supplement feed or grazing off) are stable. High input systems (System 3 and System 4) have increased from 28% to 54%. System 5 farms (using animal confinements) are increasing with time.

2.2 Off grazing facilities used in NZ

Traditionally NZ dairy farming is based on pasture grazing but due to rapid intensification of dairy farms, a variety of off paddock systems have been developed (Longhurst et al. 2006) to feed supplements to cows and protect pastures from treading damage. The most common type of off paddock facilities currently being used in NZ are; feed pads, stand-off pads, animal shelters and wintering barns. The use of stand-off pads and feed pads is widely spread in NZ (~50%) whereas the use of animal shelters and wintering barns (~3%) is increasing over time. Each structure has its own set of management strategies used for different time periods. The use of a wintering barn is a relatively new practice in NZ. Three main systems currently being used in NZ are free-stall barns, HerdHomes® and Redpath® barns (Luo et al., 2013). This research focuses on NH_3 emissions from a free stall wintering barn used for duration controlled grazing in Manawatu region of NZ. Briefly, barns are made up of; steel and iron roofs, feeding lanes, resting cubicles, walking or excreta lanes and concrete floors. The barn has rubber matting in the freestall cubicles where cows lie and rest. A typical barn provides an area of 8.5 m^2 per cow (~200 cows) and it is 70 m long x 34.2 m wide (our study case).

An automatic cleaning system with rope driven scrapers capture the manure in walking lanes and deliver it to post slurry storage pits located at the edges of barn.

As estimated by Saggar et al. (2004), in NZ around 180 million m^3 of urine and 300,000 m^3 of dung are generated by cattle daily. Likewise the effluent generated by farm dairies was estimated to be 70 million m^3, which is applied back to land for sustainable farming systems in NZ. Similarly, meta-analysis by Selbie et al. (2015) showed that a typical urine patch represents an 200 - 2000 kg N ha^{-1} after urine deposition depending on the type of livestock, age and stage of lactation and protein content of the sward. The average N loading rate in an average urine patch for dairy cows is 613 kg N ha^{-1} (Selbie et al. 2015).

2.3 Review of the processes of Ammonia gas release, emission and dispersion

2.3.1 Gaseous ammonia formation and dispersion from dairy slurry

The process of NH_3 volatilization from slurry surfaces has been described as the creation of NH_3 molecules within manure mainly through urea hydrolysis but also from the mineralisation of the organic N compounds found in urine and dung. The movement of NH_3 to the surface of slurry is achieved through diffusion followed by subsequent release to the atmosphere via turbulence and convective mass transfer through the laminar boundary layer of slurry (Teye and Hautala 2008). Volatilization is achieved through its surrogate species NH_4-N, since NH_3 and NH_4^+ exist in an aqueous environment in an equilibrium, which is governed by pH and temperature. At constant temperature the equilibrium between NH_4^+ and NH_3 is regulated by pH, a rise in pH shifts equilibrium towards NH_3 promoting volatilization. The rate of volatilization is directly proportional to the concentration of total ammoniacal N (TAN) present in slurry (Hristov et al. 2011). NH_4^+/NH_3 equilibrium is also influenced by the release of dissolved CO_2 from the slurry surface. The rapid release of dissolved CO_2 prevents the depression of the pH of the manure, thereby accelerating the process of NH_3 volatilization from the surface of the slurry (Chaoui et al. 2009). The chemical composition of slurry and the transformation processes taking place within slurry determines the concentration of NH_{3l} in TAN within the manure. Commonly urea-N in urine is the main source of TAN in mixed cattle slurry, therefore urine is considered as the main input source for estimating NH_3 emissions from any stage of manure management (Sommer et al. 2006).

2.3.2 Urea hydrolysis

Urea hydrolysis takes place in two steps; firstly diamide urea is converted into ammonium carbonate [$(NH_4)_2CO_3$)] (Eq.2.1) by urease enzyme followed by dissociation into ammonium (NH_4^+), carbon dioxide (CO_2) and water (H_2O) (Eq.2.2).

$$CO(NH_2)_2 + 2H_2O \xrightarrow{urease} (NH_4)_2CO_3 \quad \text{(Eq.2.1)}$$

$$(NH_4)_2CO_3 + 2H^+ \leftrightarrow 2NH_4^+ + CO_2 + H_2O \quad \text{(Eq.2.2)}$$

$$NH_4^+ + OH^- \leftrightarrow NH_3 + H_2O \quad \text{(Eq.2.3)}$$

As the pH of the manure solution rises the NH_4^+: NH_3 equilibria favours the release of NH_3. The presence of urease enzyme in dung plays a key role in accelerating the hydrolysis of urinary urea N. Urea hydrolysis is affected by pH and the optimum pH for animal manure ranges between 6 - 9 (Petersen et al. 1998). On average fresh dairy cow urine contains only 3% of NH_3-N whereas 80 - 90% of urinary N is urea N followed by alantoin, uric acid, creatinine, creatine and hippuric acid (Pereira et al. 2012). The activity of urease enzyme is dependent on urea concentration of the urine, pH of the slurry and temperature and it increases with temperature between 10 ^oC and 40 ^oC (Pereira et al. 2012).

2.3.3 The K_d (Dissociation constant) of NH_4^+

As discussed above, NH_3 emission rate from slurry surfaces is regulated by both slurry characteristics and environmental conditions. NH_3 is a basic gas with high affinity for water, this reaction is fundamental in determining the rate of volatilization of NH_3 gas (Freney et al. 1983). Following hydrolysis of urea, NH_4^+ converts to either $NH_{3(aq)}$ or $NH_{3(g)}$ based on acid/base equilibrium rules with pKa 9.25 at 25 ^oC (Hristov et al. 2011). The concentration of $NH_{3(aq)}$ or $NH_{3(g)}$ in a solution depends on the chemical equilibrium between both ionized ammonium (NH_4^+) and unionized ammonia (NH_3) forms of

ammonia. The NH_4^+/NH_3 equilibrium is controlled by difference in concentration of NH_4^+ within the solution along with pH and temperature of the solution (Bussink, Huijsmans, and Ketelaars 1994). The other main processes in driving volatilization rate are partial pressure above the solution which also affects the rate of removal and dispersion of NH_3 gas in the atmosphere (Freney et al. 1983; Saggar et al. 2004).

The volatile NH_3 fraction of manure is determined by the K_d of NH_4^+ and the concentration of TAN present in the manure. The proportion of TAN present as NH_3-N or NH_4^+-N in the manure cannot be measured directly (Emerson et al. 1975) but can be analysed analytically in the laboratories using colorimetric analysis (Novozamsky et al. 1983). According to (Chaoui et al. 2009) the fraction of TAN present as NH_3 can be predicted based on thermodynamic principles. NH_3 volatilization from manure surface should obey Henry's law and simple pH equilibria rules. The concentration of dissolved NH_3 in manure and in the air above the manure surface can be related using Henry's law, which indicates the partition between ionized and unionized form of NH_3 at the manure surface and air. The NH_3 volatilization flux is a convective mass transfer dependent on concentration gradient between NH_4^+ and NH_3, air flow above the gradient, ambient temperature and pH (Ndegwa et al. 2008). The equilibrium between NH_3 and NH_4^+ in the liquid phase is described by the dissociation constant, K_d, described by equation 2.3 and 2.4

$$NH_4^+ \leftrightarrow NH_3 + H^+ \qquad \text{(Eq.2.4)}$$

The NH_3 in solution ($NH_{3,l}$) is the product of the dissociation of NH_4^+ which produces 1 mol of H for each mole of NH_3 (equation 2.4). The concentration of $NH_{3,l}$ is therefore related to both the concentrations of [TAN] and [H] in the solution. Furthermore, the concentrations of $NH_{3,g}$ and $NH_{3,l}$ are affected by temperature as the equilibrium constants K_N and K_H are exponential functions of the temperature of the solution. Therefore, increasing temperature will increase the release of NH_3 from the manure. The rate at which NH_3 is volatilised is described by equation 2.5.

$$J_{NH_3} = h_m([NH_3]_{gas} - [NH_3]_{ambient}) \qquad \text{(Eq.2.5)}$$

where J_{NH_3} is the flux of NH_3 volatilization (g NH_3-N m^{-2} s^{-1}), h_m is the coefficient of convective mass transfer (m s^{-1}), $[NH_3]_{gas}$ is the gaseous NH_3 concentration in equilibrium with NH_3 in solution (g NH_3-N m^{-3} air), whilst $[NH_3]_{ambient}$ is the concentration of NH_3 (g NH_3-N m^{-3} air) in air (normally very small). NH_3 volatilization from manure surface should obey Henry's law and simple pH equilibria rules. The concentration of dissolved NH_3 in manure and above the manure surface can be related using Henry's law which indicates the partition between ionized and unionized form of NH_3 in manure surface and air given by following equation 2.6

$$[NH_3]_{solution} \overset{K_h}{\leftrightarrow} [NH_3]_{gas} \qquad \text{(Eq.2.6)}$$

where K_h is Henry's law constant (g NH_3-N m^{-3} air) / (g NH_3-N m^{-3} manure)
The relative concentration of both forms (ionized and unionized) in a medium or solution also depends on temperature.Kd of NH_4^+ in water based solution was modelled by (Emerson et al. 1975) on pKa (acid dissociation constant) using the following equation 2.7

$$pka = 0.09108 + \frac{2729.92}{273.2 + Tl} \qquad \text{(Eq.2.7)}$$

Furthermore, to estimate the fraction of unionized NH_3 based on temperature and pH of the solution Emerson et al. (1975) used the equation 2.8.

$$Un - ionized\ NH_3\ (\%)\ = \frac{100}{(1 + 10^{(pKa - pH))}} \qquad \text{(Eq.2.8)}$$

All the above mentioned processes and NH_3 emission chemistry shows that the initial urea concentration of the slurry will have the greatest influence on the initial pH and NH_4^+ concentrations of combined urine dung slurry mixtures. Typically the NH_3 emission flux from dairy cattle urine applied to soil has been characterised by high emission fluxes in

the beginning before reaching the background level with the passage of time (Amon et al. 2006; Laubach et al. 2013). The theory strongly suggests that the urea concentration of the urine plays a key role in promoting NH_3 emissions. A better understanding of the factors stimulating NH_3 volatilization from dairy cattle manure and subsequent stages of manure management will help develop mitigation strategies to minimise the emissions from the hotspots systematically.

2.4 Factors influencing ammonia volatilization from subsequent stages of manure management

The factors affecting NH_3 volatilization from dairy cattle confinements can be categorized into the following groups

2.4.1 Animal Housing

The type of building structure used is built in accordance with production objectives and local climates. Animal buildings have no direct impact on gaseous emissions but these define the methods used to handle, accumulate, process and use the manure (Montes et al. 2013). All the important factors for building structures and management policies are linked to animal wellbeing, indoor air quality and environmental pollution (Oenema, Oudendag and Velthof 2007). In most European countries loose-housing structures with liquid manure storage system are preferred over tied stall housing structures with solid manure for cattle and pig production (Sommer et al. 2006). In the summer season the floors have high emission rate because of high air temperature and ventilation rates and hence high NH_3 volatilization. NH_3 emissions in animal buildings are influenced by surface area of the dung (Jungbluth and Büscher 1996). Ni et al. (1999) showed a positive linear relationship between surface area of manure and NH_3 emissions because floor contaminations increase the surface area of manure. In Denmark and Netherlands the concentrations ranged from 0.84 g LU^{-1} h^{-1} to 1.77 g LU^{-1} h^{-1} (1 LU = 500 kg animal weight) whereas in Germany the reported concentrations were 1.62 g LU^{-1} h^{-1}. Similarly in the United Kingdom, NH_3 emissions rate was 1.02 g LU^{-1} h^{-1} in a dairy cattle house (Demmers et al. 2001). Ngwabie et al. (2009) used multi-location sampling approach to quantify NH_3 and GHG from a naturally ventilated cow barn. The indoor concentrations of NH_3 were quantified from nine locations and outdoor concentrations form two locations. They observed that NH_3 emissions peaked with increase in animal activity,

urination, defecation, mixing and removal of manure. The NH_3 emissions ranged from 0.89 - 1.19 g LU^{-1} h^{-1}, respectively. In a Swiss study (Schrade et al. 2012) reported the daily average NH_3 emission from naturally ventilated dairy free stall barn varied from 31 to 67 g LU^{-1} d^{-1} in summer, from 16 to 44 g LU^{-1} d^{-1} in the transition period, and from 6 to 23 g LU^{-1} d^{-1} in winter (1 LU = 500 kg live weight). Wu et al. (2012) modelled the influence of climatic factors on NH_3 and CH_4 emissions from two naturally ventilated dairy cattle buildings with different types of floor, manure management practices and totally different layouts. They found a diurnal variation in the NH_3 emission rates which ranged from 32 to 77 g HPU^{-1} d^{-1} and 18 to 30 g HPU^{-1} d^{-1} (in building 1 and 2, respectively), where 1 HPU (one Heat Producing Unit) is 1000W of the total heat produced by the animals at 20 ºC. They also found a significant linear relationship between climatic parameters (temperature and wind speed) and concentration of NH_3 emissions. Saha et al. (2014) studied diel and seasonal variations and associated influencing factors on NH_3 and methane emissions in a naturally ventilated dairy building). The total emissions recorded in winters were 0.33 - 1.47 g LU^{-1} h^{-1}, 0.38 - 3.87 g LU^{-1} h^{-1} in spring, 0.36 - 4.42 g LU^{-1} h^{-1} in summer and 0.23 - 2.28 g LU^{-1} h^{-1} in autumn. The impact of air movement, relative humidity and temperature on concentration of NH_3 emissions inside a naturally ventilated barn was studied by (Angrecka and Herbut 2014). During entire measuring period (one year) average level of NH_3 was 2.73 ppm which is below the defined harmful value (15 - 20 ppm) for animals.

The common aspect of all these studies is that there is a range of NH_3 emissions from ventilated barns not only depending on animal type and density of housing but also on the climate conditions different seasons and range of techniques have been used measure and estimated using range of techniques. There appears to be no data for dairy cows housed in NZ.

2.4.2 Animal diet (crude protein intake)

The main source of N in cattle diet is crude proteins; reducing N in the diet can reduce NH_3 emissions (Aneja, Schlesinger, and Erisman 2008). Under optimum conditions up to 80% of the urea in urine can be volatilized within two hours. NH_3 volatilization mainly takes place from urine (Rhoades et al. 2010). The number, age, type of storage, management routine, excretion rate of N per animal determines the NH_3 volatilization rate (Arogo et al. 2002). The physical and biochemical factors within the urine, high

urinary N per cow per day gives a high potential of NH_3 release (Cole et al. 2005). The concentration of urinary N accounts approximately 40% of total fluctuations of release of NH_3. Cole et al. (2005) investigated the effect of increasing dietary crude proteins from 11.5 – 14.5% and found increase in NH_3-N loss from 3.15% - 4.32%. They found increasing urinary N increased NH_3 emissions and conversely there was decrease in urinary N excretion with decrease in crude protein. In another laboratory incubation 44% reduction in NH_3 emissions was reported when the dietary crude protein intake was lowered from 13 to 11.5% (Todd, Cole, and Clark 2006). In another dietary manipulation trial, (Powell et al. 2008) reported NH_3 emissions were two fold higher in spring when N intake was high which resulted in high N excretions by lactating dairy cows housed in a tie-stall dairy barn. Manipulating and optimising the dietary crude seems to have largest impact in minimising NH_3 emissions from a dairy farm because it lowers the concentration of N excreted in urine. In a recent NZ study (Kyamanywa et al. 2020) studied the effect of changing late summer diet from high crude protein pastures (HCP) to medium crude protein brassica (MCP) and low crude protein silages (LCP) on urinary load on paddocks and milk production by dairy cows. These authors found a 20% reduction in urinary N loads without impacting milk production.

On rain fed pastures in NZ, the diet of dairy cows changes throughout the lactation season with energy supplements (e.g. maize silage and grains) used to complement the high crude protein content of early spring grass. As grass quality decreases in summer it is common to introduce forage crops (e.g. leafy and bulb turnips) into the diet. There is no current data on how these diet changes may influence NH_3 emissions from urine deposited in the paddock, in yards or wintering barns.

2.4.3 Slurry Storage

The cattle/animal facilities are kept clean by two common practices flushing and scraping the slurry to storage channel pits and subsequently to the storage pond. Managing large volumes of excreta deposition in an intensive farming system is challenging as it leads to detrimental environmental effects (Viguria et al. 2015). The slurry is stored in concrete ponds located beneath the barn which could be either covered or uncovered, a common practice in many countries. Different types of storage covers ranging from natural to semi permeable crusts depending on the porosity and DM content have been reported in the literature. Many factors like porosity thickness and degradability and permeability

determines the effectiveness of the cover (Misselbrook et al. 2005e). Liquid manure stores are usually covered to minimise NH_3 emissions. Reduction in NH_3 emissions has also been reported after covering the heap (Chadwick, 2005; Webb et al., 2012). Peterson et al. (2013) documented ten-fold decrease in NH_3 emissions with straw enforced crust compared to crust without straw during summer storage. van der Weerden et al. (2014) reported higher NH_3 emissions from un-inoculated storage tanks due to slow rate of crust formation. The formation of natural crust during storage is influenced by slurry characteristics such as livestock diet specially grass silage, volume to surface area ratio of the pond, slurry dry matter content and environmental characteristics such as daily evaporation rate and rainfall events (Smith et al. 2007). Another effective way of slurry handling and mitigating NH_3 emissions is by using impermeable covers (Guarino et al. 2006; Stenglein et al. 2011). Covering storage pond acts as a barrier between manure surface and wind lowering the liquid surface-air interface which restricts NH_3 release into the atmosphere (Stenglein et al. 2011). Recently in NZ, Laubach et al. (2015) did a comprehensive review on GHG and NH_3 emissions from different farming practices in NZ and provided an overview on differences in overseas and NZ farming practices. Briefly, NZ review and most of the literature (Leytem and Dungan 2014; Wood et al. 2014; Baldé et al. 2018) suggests that NH_3 gas emissions from storage ponds are highly dependent on slurry management practices for example agitation, slurry chemical characteristics and climatic conditions. Whilst GHG emissions from effluent ponds receiving farm dairy effluent (FDE) has been measured on dairy farms in NZ the extent of NH_3 emissions has not been measured (Laubach et al. 2015). It is important to quantify NH_3 emissions from storage pond to estimate the emission rate from this stage of manure management and to mitigate the emission swapping from one stage to the next one.

2.4.4 Land application

NH_3 emissions after land application of manure vary with animal (type, diets, feed conversions) and difference in manure management practices(Chadwick, Ledgard, and Brown 2002). Animal manure is a valuable source of nutrients and therefore has been used as organic fertilizer. Increase in animal population accompanied by continuous nutrients flow creates a nutrient imbalance at the farm and watershed scale leading to air and water pollution (Montes et al. 2013). The final step in manure management is the land application of manure (slurries, effluents, solids) generated by confined animals. Environmental conditions highly influence the emission of NH_3 emissions; therefore re-

introduction of manures in the environment is one of the greatest challenges in manure management. Upon land application of manure the rate of NH_3 volatilization is also affected by soil characteristics (cation exchange capacity (CEC) and pH); lower pH and high CEC lower the process of volatilization (Freney et al. 1983). Manure infiltrates rapidly through a dry soil lowering NH_3 emissions. Soil tillage also impacts volatilization of NH_3, recently tilled soil will absorb slurry rapidly because of high CEC which keeps NH_3 volatilization low (de Jonge et al. 2004). After the land application of manure, the crop increases the contact area of manure with the ambient air and act as a physical barrier against infiltration (Amberger 1990). Manure pH, dry matter content (DM) and TAN affect the rate of NH_3 volatilization (Rotz 2004). Manure is applied to land using three main techniques; band spreading, injection into the soil and broadcast spread. In band spreading system a trailing shoe system applies slurry in bands either on the top of the pasture or beneath the sward on the soil surface keeping the pasture effluent free. Broadcast spreading system can handle different types of manure (effluent, slurries) depending on the storage conditions and spreading units. The sides or back of the storage vehicle spread effluents on land. Effluents are directly injected into the soil either shallow or deep using effluent injection technique (Huijsmans et al. 2003; Rodhe and Etana 2005; Holly et al. 2017). In NZ only few studies (Li et al. 2013, 2014) quantified NH_3 emissions from farm dairy effluent application to land.

In summary the main factors influencing NH_3 loss during land application are manure type and ratio of ammonical N to total N, rate of application, surface application or incorporation into the soil, soil moisture and temperature, sward cover and subsequent rainfall or irrigation. The effect of application technique on magnitude NH_3 emissions during the land application of manure from wintering barns has not been studied in NZ.

The literature review and that conducted by (Laubach et al. 2015) has shown that there is a dearth of information on NH_3 emissions from all parts of the manure management chain associated with farm dairys , feedpads and winter barns.

2.5 Measuring ammonia gas concentrations from animal confinements

High quality data is required to study the effect of different factors on NH_3 emissions when monitoring concentrations of NH_3 to calculate emissions. Accuracy and precision of gas concentrations and airflow rates determines the quality of data (Borhan et al. 2012). The level of uncertainty in estimating the accurate emissions depends on the error associated with sampling protocol, devices and gas analysers (Ndegwa et al. 2008; Ni and Heber 2008; Shah, Westerman, and Arogo 2006). In order to develop NH_3 mitigation policies, quantification of gas emissions from livestock buildings under a wide range of production and management systems is vital.

The concentration of NH_3 in animal buildings is measured by different instruments and the choice of instrument for measuring gas concentrations depend on the objectives of the research, sampling frequency, duration of sampling, number of locations instruments are required to make measurements and the budget of the experiment (Ni and Heber 2008).

For NH_3 gas quantification, samples are usually taken from the air flowing through the animal structures on different locations and at specific times. Irregular distribution of gas production sources (urine puddles, storage pits, animals) result in spatial variations in gas concentrations inside the animal buildings (Cnockaert et al. 2007; Van Buggenhout et al. 2009). Spatial resolution can be enhanced by increasing the number of sampling locations which is dependent on the measuring instrument. The quality of data in large animal buildings also depends on choice of the most representative sampling locations (hot spots). To calculate emission rates from the animal building at least one indoor location and one outdoor location is needed. The choice of sampling location can easily be determined in a mechanically ventilated building as compared to naturally ventilated building with no defined inlets and outlets. In a mechanically ventilated building sampling locations are usually chosen at the exhaust air fans ducts and air inlets whereas air samples are taken from uniformly distributed places inside naturally ventilated animal buildings (Zhang et al. 2005).

Climate conditions (wind velocity, wind direction, temperature, humidity), ventilation rates, manure management parameters (feed, storage, manure removal), animals' activity and weight are responsible for temporal variations in gas concentrations. In animal buildings temporal variations in gas concentrations have been measured on diurnal, daily and seasonal basis (Haeussermann et al. 2006). The quality of data is improved by

measuring the gas concentrations at high frequencies to over-come short term changes within the day and for long duration to over-come daily variations. To cover seasonal variations extremely long sampling durations or intermittent quantification is required (Ni and Heber 2008).

Closed, point and open path methods are applicable for gas sampling in animal buildings (Ni and Heber 2008). Mostly flux chambers are used in outdoor manure feeding facilities, grazing areas, indoor floor areas and storage facilities for closed sampling. Point sampling is used for indoor measurements of gas concentrations inside animal buildings and outside for background concentrations (Zhang et al. 2005).

Several methods and techniques are available for measurement of gas concentrations from animal confinements (Ni and Heber 2008). All the methodologies can be classified into three main groups.

2.5.1 Wet Chemistry/ Acid traps

NH_3 gas is highly soluble in water therefore the property of adsorption and desorption NH_3 is used quantify NH_3 from enclosure and tubing walls (Hu et al. 2014). Teflon tubing has been used by many researchers to minimise NH_3 adsorption (Aguerre et al. 2011; Misselbrook et al. 2005b). Wet chemistry techniques are simple, cheap, reliable and most used for NH_3 quantification (Harper 2005). It is the best technique for estimation NH_3 by passing a known volume of air through the acid (Phillips et al. 2000). Acid traps are employed in conjugation with long term chambers. Usually sulphuric acid (0.01 - 0.2 M H_2SO_4) (Di and Cameron 2004; Luo et al. 2006; Dawar et al. 2011) boric acid (2 - 4% H_3BO_3) (van der Weerden et al. 1996; Rodríguez, Alonso-Gaite, and Álvarez-Benedí 2005) and orthophosphoric (0.002 - 0.02 M H_3PO_4) (Whitehead and Raistrick 1992; Zaman and Blennerhassett 2010) have been reported. Exposure of acid solution depends on the NH_3 gas concentration in the environment. The exposed acid solution is then analysed via colorimetric and titrimetric methods in the laboratory (Ndegwa et al. 2009).

2.5.2 Ammonia Denuders

Several passive adsorption devices (gas detection tubes, filter packs, diffusion samplers) use a solid acidic surface (organic acids or phosphoric acid) protected by a membrane from air turbulence to capture NH_3 from air (Sommer, Schjoerring, and Denmead 2004;

Ni and Heber 2008). Usually oxalic acid ($C_2H_2O_4$) is applied with an acetone and citric acid ($C_6H_8O_7$) as solvents and phosphoric acid (H_3PO_4) and tartaric acid ($C_4H_6O_6$) are applied with methanol as a solvent (Shah et al. 2006). Tubular denuders (Ferm tubes) can be categorised into active and passive samplers (Shah et al. 2006). For active sampling vacuum pump is used for the continuous flow of air into the tubes while passive samplers depend on natural air flow (Ni and Heber 2008). Passive samplers also called as "shuttle" are often used in micrometeorological technique in field studies (Sherlock et al. 2002; Huijsmans 2003; Laubach et al. 2013). NH_3 flux can be directly measured via shuttles because the air flow through the sampler is directly proportional to wind speed (Leuning et al. 1985). Active sampling tubes are needed for real time measurements at animal facilities. Drager tube is the most popular active sampling device with a manual pump to draw air. The NH_3 estimations are based on colour change (Ni and Heber 2008).

2.5.3 Optical methods

Optical devices quantify NH_3 concentration in the air by assessing the interaction of NH_3 molecules and electromagnetic radiation. This technique can be categorized into three main groups: Chemiluminescence, fluorescence and spectroscopy (Ni and Heber 2008).

2.5.4 Farm scale balances

This technique is used in animal houses, to determine the emission rate by calculating the difference between inlet and outlet NH_3-gas fluxes assuming the stationary conditions.

$$E_i = F * (C_{s(i)} - C_{e(i)}) \qquad \text{(Eq.2.9)}$$

where Ei = emission rate of the gas (mg h^{-1})

F = ventilation rate (m^3 h^{-1})

$C_{s(i)}$ = incoming NH_3-gas concentration (mg m^{-3})

$C_{e(i)}$) = outgoing NH_3-gas concentration (mg m^{-3})

This technique was evaluated by (Bottcher et al. 2000; Koerkamp et al. 1998) to calculate gaseous emissions from swine building and from livestock buildings in Europe.

2.5.5 Chamber approaches

Chamber are used commonly for quantifying NH_3 emissions from dung patches, manure samples or composting areas (Hu et al. 2014). These methods, used for quantifying

gaseous emissions directly from soil and manure, provide portability and sensitivity (Denmead et al. 1998). Many studies investigated NH_3 emissions from manure but experiments have quite often been conducted in laboratory or field (Misselbrook & Powell, 2005; Pereira et al. 2012). In field studies chambers have been used for measuring emissions from soil, dung pats and composting manure (de Klein et al. 2003; Chadwick 2005).

There are two types of chambers (static and dynamic) used for measuring NH_3 emissions from emitting sources or surfaces (animals or manure) based on a mass balance principle. In static chambers, emissions are calculated by the rate of increase of concentration of gas after the sample has been enclosed by the chamber. For estimating emission rates, a linear regression approach is used from a number of samples during set measurement period (Külling et al. 2001). According to de Klein et al. (2003) non-linear increases in gas samples can be identified by taking a minimum of three samples during the measurement period. Chamber methods are more sensitive as compared to other methods for quantifying NH_3 from agricultural systems (Hu et al. 2014). In case of dynamic chambers, a known rate of air is exchanged with the exterior atmosphere with vacuum pump system. The air passed through the chamber is captured by the acid trap which is used for calculating NH_3 flux over a period of time (Zaman and Blennerhassett 2010).

2.5.6 Micrometeorological (MM) techniques

MM techniques are commonly used to quantify multiple gases (CH_4, NH_3, N_2O) from both point and non-point sources (Hu et al. 2014). These techniques are truly in situ, offering advantages over chamber techniques (static, dynamic) and integrating fluxes over larger areas (Brown, Wagner-Riddle, and Thurtell 2002). MM techniques assume uniform and homogeneous air flow and measurements are based on mass balance considerations, flux gradient relationships or dispersion modelling (Harper et al. 2004). Micrometeorological techniques measure the emissions from the source without disturbing the measurement environment. This technique allows the measurement of gas fluxes over a larger surface than chamber techniques. Meteorological data for example, wind speed profile, temperature, humidity, air pressure is used to calculate the emission fluxes from the source (McGinn et al. 2007). MM balance approach is considered the standard method for quantification of NH_3 volatilization. MM techniques have been further divided into following classes

i) Eddy Covariance Method (EC)

EC is the only method measuring the turbulence transfer directly from the emitting source. The variation in gas concentrations is measured by vertical flow of wind (discrete air parcels) called eddies over a large emitting area (Foken, Aubinet, and Leuning 2012). Gaseous flux is calculated by:

$$F_g = C'.w \quad \text{(Eq. 2.10)}$$

F_g is the rate of emission, C' is fluctuation measured in gas concentration and w is the speed of vertical wind or air flow (Ferrara et al. 2012). Practical application EC approach needs expensive equipment to monitor metrological data (temperature, water vapour flux, heat flux) to obtain accurate results (Hu et al. 2014).

i) Integrated Horizontal Flux (IHF) Method

The IHF approach quantifies the horizontal flux of NH_3 at different heights to determine the vertical flux for the total emission of NH_3. When the air flows over an emitting source (e.g. manure storage pond or after land application of effluent) NH_3 diffuses into the air stream from the emitting source (Hu et al. 2014). The air flow rate and NH_3 concentrations are measured at different heights above the source using anemometers and NH_3 traps, respectively. The IHF approach has been used to measure emission of gases from grazing cattle, feed lot cattle and manure storage facilities (Koenig, McGinn, and Beauchemin 2013). This technique has further been elaborated in section 7.2.2.3 of Chapter 7.

2.5.7 Measurement of NH_3 concentrations and Ventilation rates in barns

In cow barns the quality of emission data also depends on measurement of ventilation rates as well as measuring NH_3 concentrations using traps. The standard procedure for measuring ventilation rates from mechanically ventilated animal buildings is quantification of air speed with hot wire or fan wheel anemometers (Hinz and Linke 1998). The internal and external climate conditions have direct impact on ventilation rates in naturally ventilated (NV) buildings. The air inlets and outlets in a NV building depend on wind direction and thermal buoyancy.

2.5.7.1 Estimating the airflow rates using tracer

Ventilation rates can be monitored either directly or indirectly and it is very important to obtain ventilation rates from animal houses (Demmers et al. 2001). In direct approach over all ventilation rate of the building is obtained by measuring the rate of airflow from

all the openings in the house. In the case of the indirect approach a tracer gas (carbon dioxide, CO_2) is used to measure the ventilation rate. A known quantity of trace is released in the house and tracer concentration is measured inside and outside the building to calculate the ventilation rate.

Many factors like porosity thickness and degradability and permeability determines the effectiveness of the cover (Misselbrook and Powell 2005)

2.6 Conclusions

The following conclusions could be drawn from the literature review described above:

i) NH_3 gas is generated during all the stages of manure management (housing, storage, land application)

ii) Temperature (indoor and outdoor), wind speed, solar radiation and humidity, animal age, size, activity, number and manure management practices have a strong impact on the NH_3 emission profile in a naturally ventilated dairy cattle building.

iii) NH_3 generation and mechanism processes are well understood qualitatively but still there are large uncertainties associated with the quantitative aspect especially in NZ.

iv) The choice of sampling location and duration of sampling enhance the possibility of measuring representative ammonia emissions inside the naturally ventilated building.

v) The concentration of ammonia emissions vary spatially and temporally in naturally ventilated dairy cattle buildings.

vi) The lack of NZ specific data both at laboratory and field scale limits the develop ment of mitigation technologies and policy making. Understanding NH_3 emission mechanisms and emission rates facilitates the development of long term mitigation strategies.

Therefore the main objectives of this thesis were to develop methods that are appropriate to measure NH_3 volatilization losses in following situations:

1. Study the influence of slurry (urine : dung mixtures) characteristics on NH_3 emissions.
2. To measure the effect of diet on urine and dung characteristics and subsequent NH_3 emissions.

3. To measure NH_3 emissions from a freestall barn.
4. To measure NH_3 emissions from manure storage pond.
5. To measure NH_3 emissions from land application of stored manure.

Chapter 3

Development and evaluation of methods for measuring ammonia gas emissions during manure management stages

3.1 Introduction

Ammonia (NH_3) emissions from animal excreta and stored manure are classed as an indirect source of nitrous oxide emissions, a potent greenhouse (GHG), and contribute a significant proportion of N loss from housed dairy production system. New Zealand (NZ) is a signatory to the United Nations Framework Convention on Climate Change (UNFCCC) and Paris 2015 Agreement and as such is required to report GHG emissions. Country specific emission factors can be developed for Tier 2 and 3 and included in the National GHG inventory system for Agriculture (Ministry for the Environment 2016). Currently NZ's GHG inventory lacks country specific information on NH_3 emissions from NZ dairy systems that include cow housing (e.g. barn systems). In order to compile the national inventory for the range of dairy production systems, data are crucial to calculate the amount of gases emitted. In NZ very little or no data is available on NH_3 emissions from cow housing, storage and land application of animal excreta (Ministry for the Environment 2016).

This Chapter reports the evaluation and calibration of common methods that are later used in the experimental chapters. The following sections of this chapter explore the evaluation and adaptation of techniques used in experimental studies to identify the hotspots of NH_3 emissions from each emitting source (excreta deposition on barn floors, floor scraping schedule, storage channel pits, storage pond and re-application of manure to land). In NZ very limited work (van der Weerden et al. 2014) has been done on quantifying NH_3 volatilization losses from dairy cow housing or standoff facilities. In order to quantify and estimate these losses it is important to develop low cost and effective NH_3 measurement techniques. Therefore, the main objectives of this chapter were;

- To evaluate, standardise and develop low cost and effective techniques for measuring NH_3 volatilization losses from various sources and stages of manure management

- To test the developed technique firstly in the laboratory and then in the field (manure storage pond and land application of manure)

  Two approaches for measurement of NH_3 emissions have been investigated; active and passive NH_3 sampling (i) in enclosures (chambers) ii) under field conditions. All methods involved trapping NH_3 in 0.5 M H_2SO_4 and determination of NH_4^+ concentrations colorimetrically using auto analyser.

3.2 Standards and reagents

Active and passive acid samplers for measuring the concentration of NH_3 gas were developed and tested with air containing a range of known concentrations of NH_3 gas. The known concentrations of NH_3 gas were produced by mixing standard grade ammonium chloride (NH_4Cl) and sodium hydroxide (1 M NaOH) in enclosures of known volume. The efficiency of NH_3 captured in sulphuric acid traps (0.05 M and 0.5 M H_2SO_4) was determined by measuring the concentration of NH_4^+ in the acid after exposing the solution to the known concentrations of NH_3 gas over different time periods. All solutions were prepared using deionised (DI) water.

3.2.1 Analytical Method

Sub samples (3 ml) were taken from the 0.5 M H_2SO_4 solution in acid traps or from the 0.05 M H_2SO_4 used to elute glass microfiber filters. The NH_4^+ concentration in the dilute acid solutions was measured by Technicon auto analyser (Novozamsky et al. 1983) with a detection limit ranging between 0.25 to 12 µg NH_4^+-N ml^{-1} for active sampling traps and 0.025 to 1.2 µg NH_4^+-N ml^{-1} for passive sampling traps. Furthermore standard NH_4^+ solutions were prepared in the respective matrix solutions to create the standard curves for each of the dilute sulphuric acid trapping solutions.

An example of the standard curve required to interpret the low concentration ranges found in passive acid traps is shown in Figure 3.1. The low concentrations of NH_4^+-N in solution required the sensitivity of the Technicon spectrophotometer was adjusted to produce significant absorbance values for a range of standard calibration solutions made up in the 0.05 M H_2SO_4 matrix. The results of the increased sensitivity calibration were successful producing a highly linear calibration curve from 0.025 to 1.2 µg ml^{-1} with a high R^2 value (Figure 3.1).

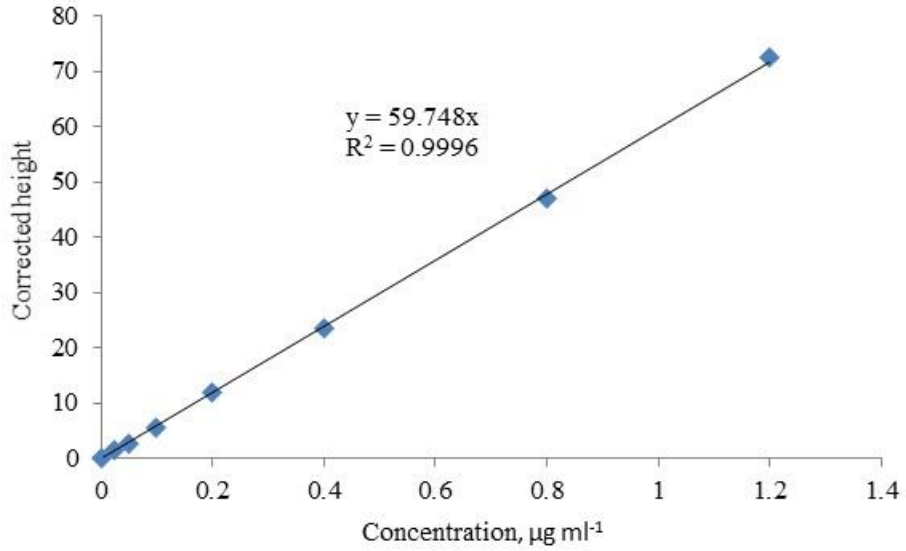


Figure 3. 1: The relationship between corrected peak height (minus baseline) and the concentration of NH_4^+ in standard solutions (colorimeter adjusted for measuring low concentrations of NH_4^+).

The % NH_3-N recovery of acid traps was calculated using the formula.

$$AR = (A_c / A) \times 100 \qquad \text{(Eq.3.1)}$$

Where, Ac= NH_4^+ - N (mg-N) trapped in the acid, A= NH_3-N (mg-N) added to the enclosure

3.3 Data evaluation

Data obtained from the calibration of active and passive samplers was evaluated by performing regression algorithms using Microsoft Excel 2013 software.

3.4 Description of ammonia measurement methods

3.4.1 Laboratory measurements

3.4.1.1 Active ammonia sampling from excreta deposition (manure surfaces) using enclosures

Background

NH_3 can be released from various sources (urine, dung, manure heaps, animals), which causes spatial variations in gas concentrations (Ngwabie et al. 2009). Temporal variations in the NH_3 gas concentrations are driven by animal activity (diet, urination, defecation), indoor and outdoor climatic conditions (wind speed, wind direction, air temperature and relative humidity) and management practices (diet and scraping schedule) (Ngwabie et al. 2009). It is hard to define air inlets or outlets in a naturally ventilated barn due to several openings which could serve as either air inlets or outlets depending on the external climatic conditions. Enclosures placed over known excreta surface areas are the most practical way of quantifying temporal change in the rate of NH_3 emissions (McGinn and Janzen 1998).

The enclosure method consists of a laboratory set up of static or dynamic chambers (Figure 3.2), which have been well established and used by (Singh, 2007) to quantify NH_3 emissions from cattle urine and fertilizer inputs. Misselbrook et al. (2005d) and Pereira et al. (2012) used a similar set up of laboratory chambers to measure NH_3 emissions from excreta deposition under laboratory conditions. Therefore the main aim of using this system was to evaluate the efficiency of this technique to measure NH_3 emissions by simulating excreta deposition on barn floor. Below the methods are discussed in the order each technique was evaluated, modified, developed and adopted.

3.4.1.2 Static/dynamic chambers set up and operation

The laboratory or in situ set up of static (or dynamic) chambers (Figure 3.2) consisted of 10 chambers (diameter 25 cm and height 15 cm) manufactured from drainage grade 250 mm PVC pipe and sealing inspection lids. (3 replicates for each treatment and 1 chamber were used as blank). Sources of NH_3 emissions, such as urine, can be placed in or covered by a chamber. Each chamber has an inlet and outlet, inlet was connected via 10 cm long

(3.2 mm diameter) tubes to a compressed air supply and the outlet was connected to 1 L dreschel bottle containing 250 ml 0.05 M H_2SO_4 acid. All the experiments for standardization and for simulating manure deposition were conducted at room temperature 18 ºC - 24 ºC.

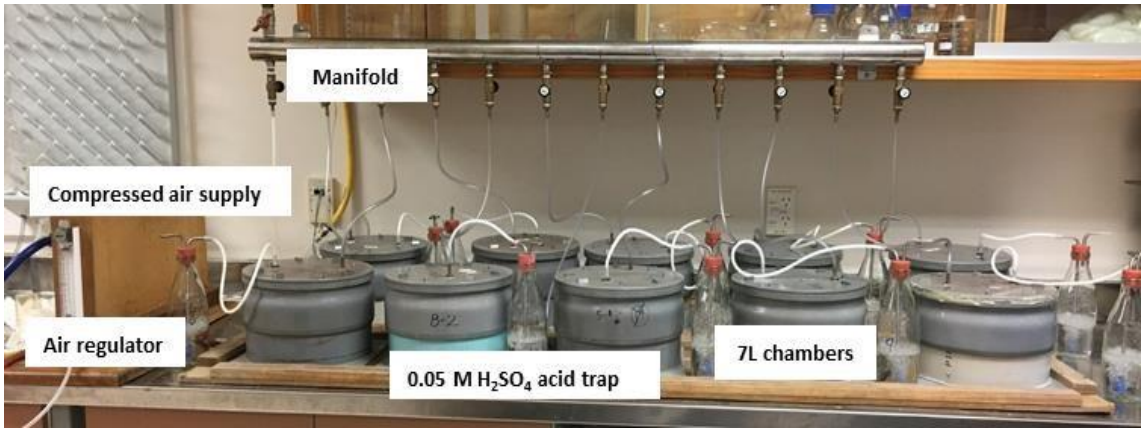


Figure 3. 2: Dynamic chambers with active flushing to acid traps in dreschel bottles set up in the laboratory

3.4.1.3 Standardising procedures for flushing dynamic chamber enclosures

Active sampling of NH_3 gas was achieved by pumping either humidified or dry air through an enclosed chamber containing an NH_3 source and allowing the exhaust air to pass through a bubble trap of acid. Known amounts of NH_3 gas (amounts of NH_3 added) were generated in the chamber by reacting NH_4Cl with excess 1M NaOH (15 ml) in a petri dish placed inside the chamber. The chambers were standardised for low (2.5 to 50 mg) and high concentrations (0.4 to 0.8 g) of NH_4^+-N used as source. At the end the alkaline solutions were neutralised with 20 ml 0.5 M H_2SO_4. For active collection of NH_3 different air flow rates (2, 4, 8 L min^{-1}) were passed through the approximately 7.0 L PVC chambers for 2 h.

3.4.1.4 Results

Table 3. 1: The amount added as NH_4Cl and estimated amount transferred and recovered as NH_3-N

Amount added as NH_4 Cl (mg N)	Amount transferred as NH_3 gas (mg N)	N recovered as % NH_3-N transferred
0.25	0.075	52
0.50	0.143	51
1.00	0.232	62
104.69	22.58	100
157.04	36.44	92
209.38	43.60	100

The total amount of NH_3 recovered at the end of the experiment from acid solutions ranged from 51 to 100% for high concentrations (Table 3.1). Amount transferred as NH_3 gas increased with increasing the concentration of the amount added as N. It was found that air flow rate had no effect on the transfer of NH_3 from the alkaline solution (source) to the acid trap. Even at the lowest rate 2 L min^{-1} the chamber air would have been replaced 17.14 times. A standard "sweeping flow rate of 4 L min^{-1} was adopted for all subsequent calibrations of enclosed chambers.

3.4.1.5 Evaluation of the closures using urine and dung mixtures over 144 h

A laboratory incubation using urine and dung (slurry mixture) experiment was performed using enclosures. The main aim of this experiment was to access the use of humidified and dry air. Two sets of 5 chambers were used, for an individual set 4 chambers had urine and dung slurry mixtures (23 g) placed in a petri dish (surface area = 0.0056 m^2) and one chamber was used as blank. Urine and dung (1.3 : 1; urine : dung) samples taken from the dietary trial (refer chapter 4 and 5) were used to make a HUN (High Urinary N) slurry containing 4692 TKN (total kjeldahl N, mg N L^{-1} and a LUN (Low Urinary N) slurry containing 3618 TKN (mg N L^{-1}). Compressed air was humidified by passing it firstly through a dreschel bottle containing 250 ml of tap water and then through the chamber

whereas compressed air flushed directly through the chambers was referred as dry chambers.

3.4.1.6 Results

The results of NH_3 emission flux from wet and dry chambers are presented in Figure 3.3. Sweeping wet air through chambers recovered 15% and 20% of the total N as NH_3-N from urine and dung slurry mixtures containing low (LUN) and high (HUN) urine N concentrations, whereas dry air sweeping caused the slurry mixtures to dry out and only 9% and 15% of the total slurry N was recovered as NH_3-N from the low (LUN) and high (HUN) slurry mixtures. Briefly, the emission flux was higher from the chambers swept with moistened air compared to dry chambers although same amount of TKN was applied (Figure 3.3). Enclosures are one of the most widely used techniques for estimating NH_3 volatilization losses.

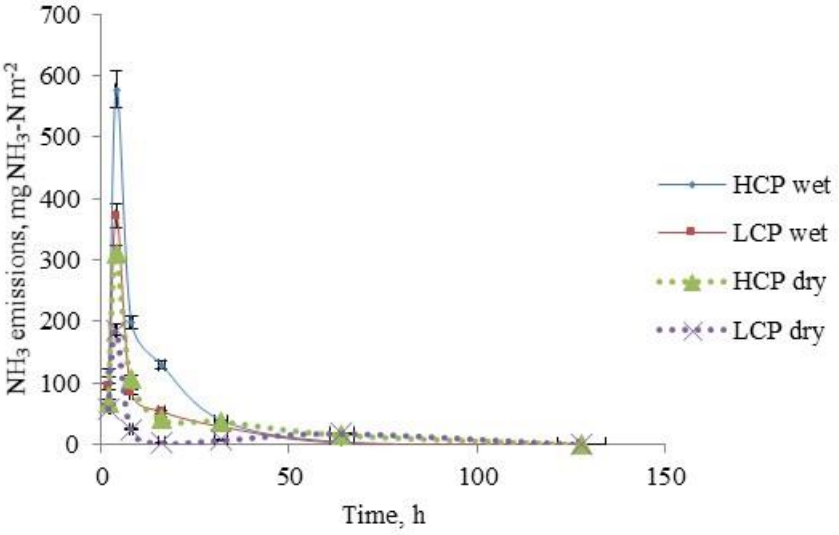


Figure 3. 3: NH_3 emission flux from slurries of urine and dung (HUN and LUN are sources with 4691 mg N L^{-1} and 3618 mg N L^{-1}, respectively) in (i) chambers swept with dry air (dotted lines) and (ii) chambers swept with humidified air (solid lines) at 4 L min^{-1} for up-to128 h

3.4.1.7 Conclusions

Air flow rate did not appear to impact rate of NH_3 emissions from the source. It was found that compressed air dries the slurry sample and reduces the efficiency of NH_3 collection from slurry mixtures. Furthermore, it was concluded that moistened air should be used to sweep dynamic chambers when measuring NH_3 emissions from urine and dung sources.

3.4.2 Low cost technique for sampling atmospheric ammonia gas in the barn: The gas sampling bag (GS- bag) technique

3.4.2.1 Background

The main objective to develop this technique was to standardize a low cost and effective method that could be used for point sampling of contaminated air in the barn (slurry, barn floor, storage pits etc). Initially, the sole purpose of this technique was to spot sample contaminated air in the barn by using a large syringe or airbed hand pump to fill the 8 L gas sampling bags (GS-bags) rapidly before they were returned to the laboratory for NH_3 analysis. The GS-bags developed, however, were also used to hold NH_3 gas standards for use in developing other low cost technique for active and passive sampling of NH_3 gas in the field experiments.

3.4.2.2 Standardisation Method

The gas sampling bags (GS-bags) were made, standardised and calibrated in the laboratory. The bags were made in the laboratory using home vacuum packaging system and FoodSaver® bags (28cm x 540cm). The laboratory set up (Figure 3.4) for testing the recovery of NH_3 from gas samples collected in the GS-bags consisted of NH_3 generation bag (Bag A), 0.3 L Syrman genia® syringe and a gas collection bag (Bag B). First of all the bags were fully evacuated by using the evacuation pump installed in the laboratory and then Bag A was accurately filled with 8 L of atmospheric air collected from the laboratory using 0.3 L Syrman genia® syringe. Then known concentration of ammonium chloride (NH_4Cl) and () 1M sodium hydroxide (NaOH) solution was injected using 10 ml syringe into the Bag A to generate NH_3 gas, the bag was left for one hour to attain equilibrium. After one hour, 6 L of air containing NH_3 gas from Bag A was transferred carefully using Syrman genia® 0.3 L syringe to another 8L Bag B containing 5 ml of 0.5 M sulphuric acid (Figure 3.4). The NH_3 gas present in the transferred air was captured in the acid which was analysed using colorimetric analysis (Novozamsky et al. 1983). It is important to maintain that only 6 L of air was transferred from the Bag A in order to avoid the moisture transfer to Bag B.

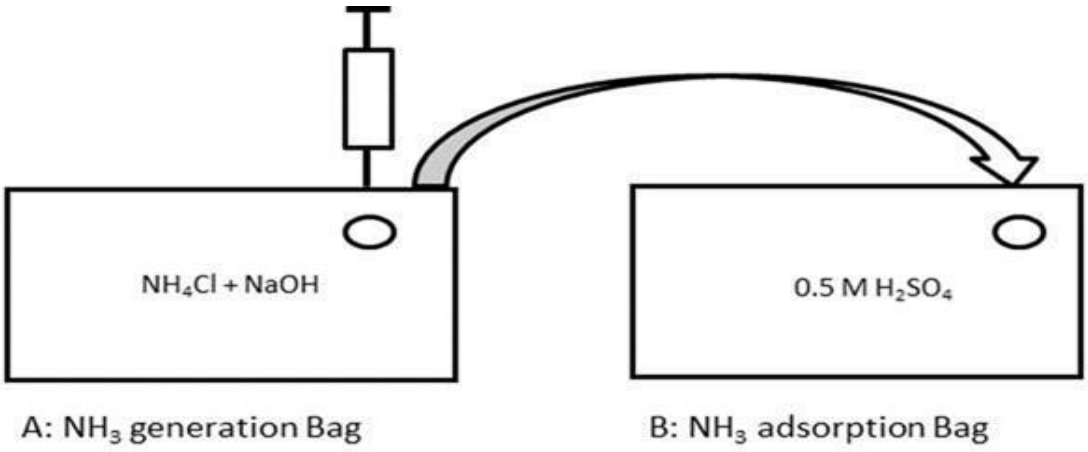


Figure 3. 4: Schematic representation of the bag technique NH_3 generation and calibration of emission measurement in the laboratory

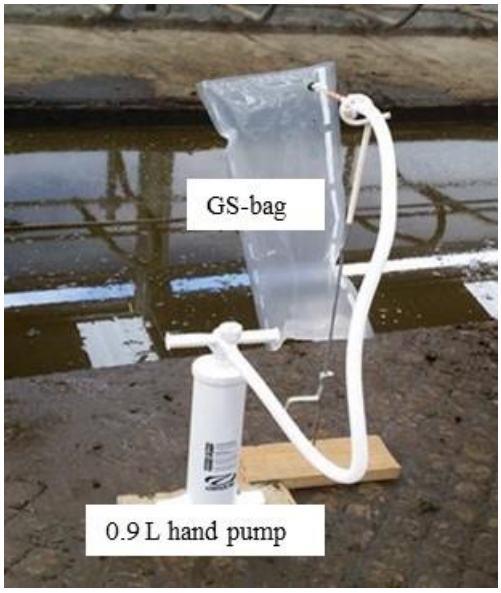


Figure 3. 5: Spot sampling of NH_3 gas in the barn using hand-pump and GS-bag

At the end of the experiment, residual NH_4^+-N concentration in the alkaline NH_4Cl and 1M NaOH solution was measured by adding 15 ml of 0.5 M H_2SO_4 making total liquid volume of GS-bag. Finally, 3 ml aliquots were taken from the total volume of liquid in the bag for colorimetric analysis. The amount of NH_3-N transferred was estimated as the difference between the known amount of NH_4Cl added to the generation bag and the residual amount of NH_4^+-N in the alkaline NH_4Cl and 1M NaOH solution.

3.4.2.3 Results

In preparing the NH_3 emission source standards it was found that when NH_3 is released from the NH_4Cl and NaOH mixture only 15 to 20% was emitted as NH_3 gas and 80 to 85% of the NH_4-N remained in alkaline solution (Figure 3.6). The transfer of NH_3 gas from the bag to the acid traps ranged from 72.62% to 102.51% based on various NH_4^+-N input levels (0.25 µg to 100 µg).

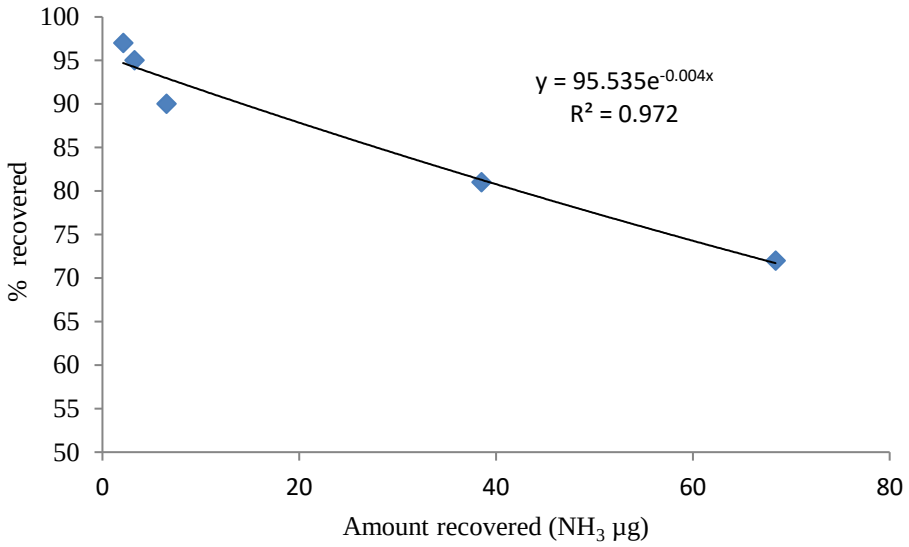


Figure 3. 6: % recovery of NH_3-N from GS-bag with low and high concentrations of NH_3 used for trapping in 0.5 M H_2SO_4 acid contained in GS-collection bag

3.4.2.4 Conclusion

The GS-bags are low cost, simple to make but extreme care needs to be taken during the whole gas transfer process. Still, the simplicity and reproducibility offers advantage for spot sampling NH_3 gas in the barn. The GS-bags were standardised for adsorbing low concentrations of NH_3 in the air. The technique worked well for low concentrations of NH_3 but when tried for high concentrations the recovery of gas transferred was low becauseas there was a problem losing NH_3 during transfer.

3.4.3 Active ammonia sampling from the barn, manure storage and land application/Dynamic acid scrubbers

Background

Chambers (enclosures) are well suited for studying NH_3 volatilization losses by simulating the manure deposition within the chamber and comparing the emissions from various sources but it was practically impossible to use these chambers in the operational freestall barn, or over the storage pond. Therefore the next step was to develop small, portable NH_3 acid traps to quantify NH_3 gas concentrations in the field.

3.4.3.1 Method

To accomplish this objective, low cost aquarium pumps (Aqua One®) were evaluated as constant flow gas samplers feeding air to 50 ml polyvinyl chloride (PVC) falcon tubes engineered as acid filled bubble traps (Figure 3.7). Firstly, the falcon tube acid scrubbers were standardised in the laboratory by using the aquarium pump to draw air of a known NH_3 concentration from an 8 L GS-bag, through a moisture trap to the acid scrubber. The test procedure was to use a 0.9 L ozone® hand-pump to quickly fill the 8 L of atmospheric air in the gas generation GS-bag. The bag was firstly connected to a wet trap to capture moisture if any and then to an aquarium pump having an inlet and outlet. The inlet of aquarium pump was connected to the wet trap while the outlet was connected to the acid trap A (10 ml 0.5 M H_2SO_4) connected likewise to a second acid trap B (10 ml 0.5 M H_2SO_4) (Figure 3.8). Then known concentration of 1M NaOH solution and various concentrations of NH_4Cl solution were introduced into the gas generation bag via 10 ml syringe. The GS-bag was left for one hour to attain equilibrium finally the aquarium pump was turned on to draw NH_3 gas from the bag to be captured by the acid traps (Figure 3.8). Two in line acid traps were used to test the efficiency of the traps.

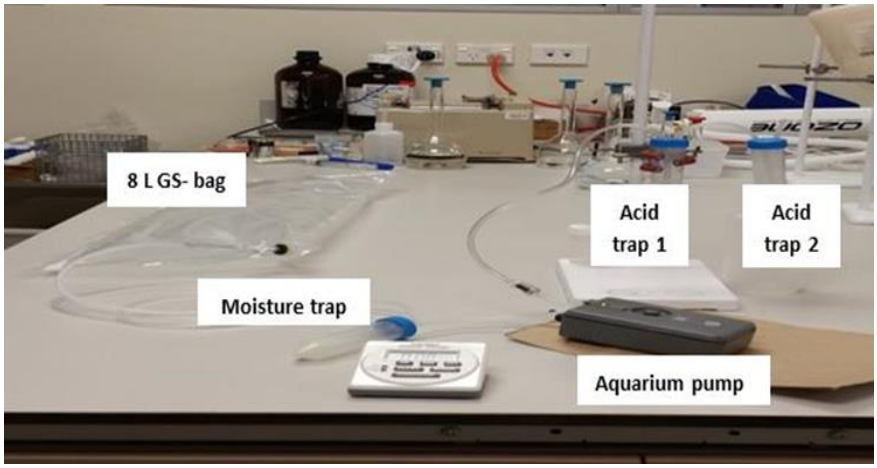


Figure 3. 7: Laboratory set up for standardising acid scrubbers for field measurements of NH_3 gas

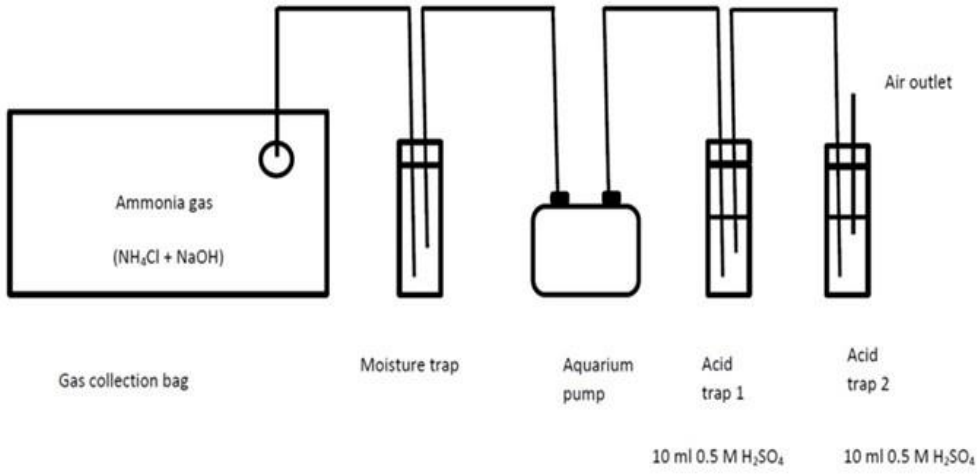


Figure 3. 8: Schematic representation of standardising portable chambers set up and operation

3.4.3.2 Results

Table 3. 2:The amount added as NH_4Cl and estimated amount transferred and recovered as NH_3-N

Amount added as NH_4 Cl (µg N)	Amount transferred as NH_3 gas (µg N)	N recovered as % NH_3-N transferred
250	71.9	68
500	111.1	70
1000	166.7	81

The concept of active NH_3 sampling and standardization was same as explained in section 3.4.2 except for replacing the chambers with 8 L - GS bags, compressed air supply with an aquarium pump and dreschel bottles with 50 ml falcon centrifuge tubes to be used as acid traps or scrubbers. The amount of %NH_3-N transferred ranged from 68 - 81% (Table 3.2). Total recoveries from both alkaline and acid solutions at the end standardization ranged from 90 - 97%. Acid trap A efficiently recovered all the released NH_3 from the source and no traces were recovered in the second trap.

3.4.3.3 Conclusions

It was concluded that active acid scrubbers can easily be used for sampling air concentrations of the NH_3 gas. These are simple, cheap, handy and portable. (Refer chapter 6 and 7 for implementation and details). One acid scrubber was found efficient for capturing NH_3 gas under laboratory and field conditions.

3.5 Passive ammonia sampling from the barn, manure storage and land application of manure

Two passive sampling techniques were tested and validated : i) passive acid traps and ii) diffusion sampling tubes embedded with acid coated filter paper to measure NH_3-N losses under laboratory and field experiments.

3.5.1 Using glass preserving jars (Agee) to test acid traps for ammonia sampling from barn floor, manure pits and storage pond

Background

3.5.1.1 Standardization with NH_4Cl solutions

Simple acid traps used for passive NH_3 sampling were tested using known amounts of NH_3 gas generated into 11 air tight 1 L glass preserving Agee jars with removable lids. A 10 ml aliquot of 0.5 M H_2SO_4 solution contained in 50 ml polyvinyl chloride (PVC) vial (passive acid trap) was placed in slanting position at the bottom of the preserving jars supported by laminating sheet with holes (Figure 3.9). The adsorption efficiency (discussed in section 3.6) of the passive acid traps in the laboratory was standardised using low and high concentrations of NH_3 released from the addition of 1 M NaOH to a

solution of NH_4Cl. The concentration of NH_4 present in the 0.5 M H_2SO_4 trapping solution was then analysed using colorimetric analysis.

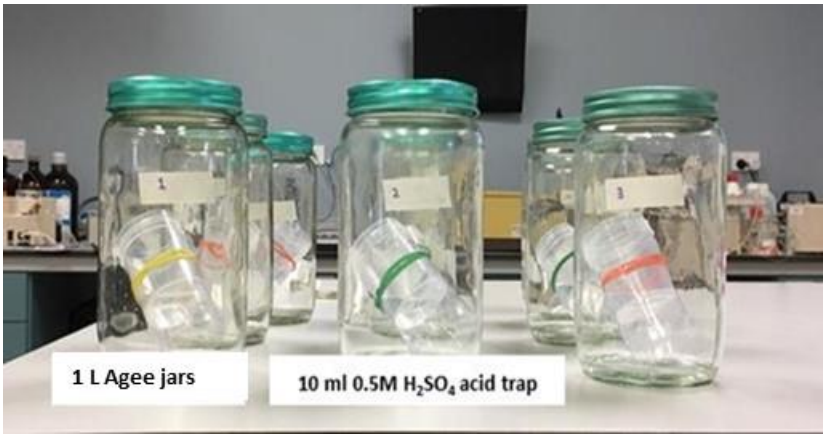
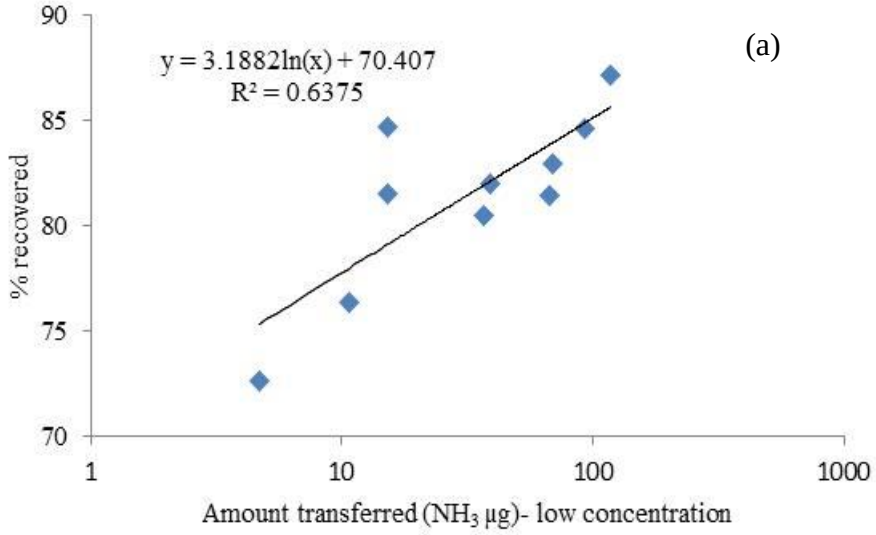


Figure 3. 9: Evaluating the efficiency of 10 ml 0.5 M H_2SO_4 acid traps contained in 50 ml PVC vials placed in 1 L Agee jars: laboratory set up

3.5.1.2 Results

Recovery of NH_3 from with NH_4Cl solutions

The efficiency of the NH_3 adsorption in the acid traps was estimated based on amount of NH_3 gas captured in the acid as a % of the actual amount transferred as NH_3 gas. Data for a wide range of NH_3- N source concentrations is presented in Figure 3.10 (a & b). The percentage of NH_3 captured in the passive traps ranged from 66 to 102% of the added NH_3 source. The percentage recovery was dependent upon the concentration of NH_3 in the standard source.



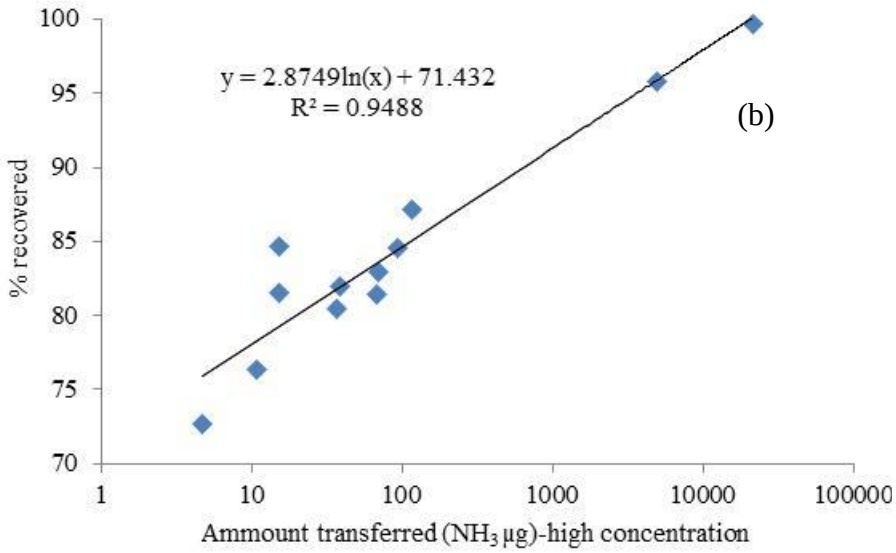


Figure 3. 10: % recovery of NH_3-N from source with (a) low and (b) high concentrations of NH_3 used for standardising 50 ml PVC passive vial containing 10 ml 0.5 M H_2SO_4 acid traps under laboratory conditions

Comparison of the efficiency of NH_3 collection from slurries by dynamic enclosures and the passive preserving jar technique

The dynamic chambers were set up with slurry HUN and LUN samples as described in Sections 3.4.1.4 and 3.4.1.5. Similar amounts of the HUN and LUN slurries were applied to the base of preserving jars and 10 ml 0.5 M H_2SO_4 acid traps contained in 50 ml PVC vials placed in 1L jars. The acid traps were replaced after 2, 4, 8, 16, 32, 64 and 128 hours and NH_4^+ concentrations in the trapping acid measured as described earlier.

When the same amount of and concentration of TKN was applied as slurry mixtures to passive acid trapping in jars and dynamic chambers (swept with moistened air) the passive traps recovered 80 - 90% of the NH_3-N recovered by the dynamic chambers after 64 h (Figure 3.11). However for shorter collection times the rate of collection by the passive acid traps was much slower and their efficiency of collection compared to dynamic chambers at 4, 8, and 16 hours was 8, 27 and 41%, respectively. Sweeping air through the chamber maintains a low ambient NH_3 concentration and accelerates the process of volatilization from the source compared to passive sampling which allows a NH_3 concentration gradient to develop form above the source.

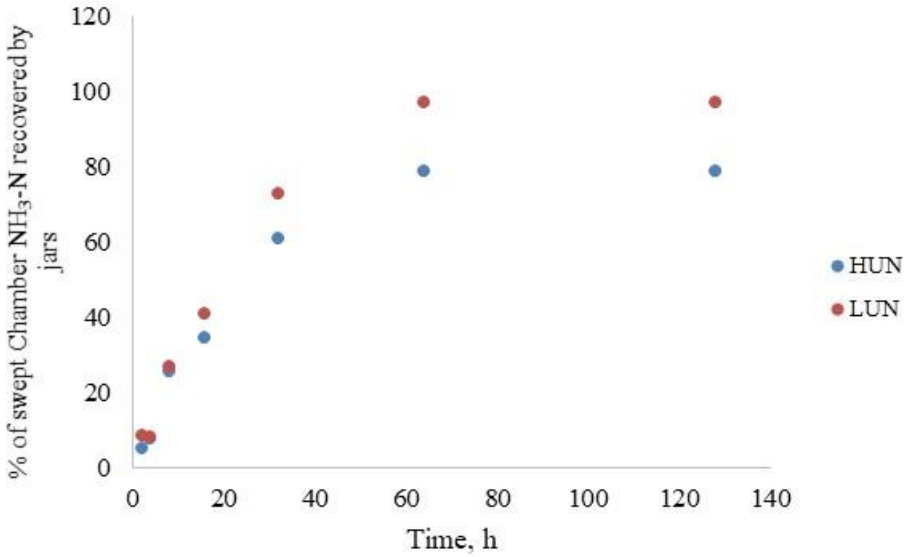


Figure 3. 11*:* %NH_3-N recovered from HUN and LUN applied to 1 L preserving jars and chambers swept with compressed air (wet and dry) at the end of experiment (128 h)

3.5.1.3 Conclusions

Preserving jars (1 L) as enclosures with 10 ml 0.5 M H_2SO_4 acid contained in 50 ml PVC vials (as acid traps) was proven to be a low cost, efficient and reliable technique for measuring relative emissions from urine, dung and manure slurries. It is clear that if enclosures are used to simulate the actual NH_3 emission from slurry cover surfaces in barn laneways or yards then the ventilation rate of the surface will also need to be simulated in the enclosure. Ventilation rate differences between enclosures and the real situation will lead to over or under-estimation of NH_3 losses from slurry covered surfaces. This is discussed further in Chapter 6; Section 6.4, where the aim was to estimate the actual NH_3 loss from a freestall barn.

Active PVC chambers will be able to estimate the total NH_3 loss from a source sample more rapidly than a passive acid trap in a preserving jar. However, dynamic chamber systems each with dreschel bottles and pumps were not suited to simultaneously analyse the large numbers of dairy cow urine, dung and mixed urine-dung slurries requiring emissions measurements. These were replaced with passively sampled 1L glass preserving jars (See section 3.51; Agee jars) which were used to address the issue of needing many enclosures (chambers) running at once to cope with the treatment and replicate numbers required in each experiment.

3.5.2.1 Description of the diffusion sampling tubes (DSTs)

Passive NH_3 sampling is based simply on the principle of diffusion of gases from source (high concentration gradient) onto an adsorbing medium (Microfiber filters in this study) along the dimensions of the tube. A passive flux sampler for adsorbing NH_3 simply consisted of 10 ml polyvinyl chloride (PVC) tubes (internal diameter 13.5 mm) secured at the bottom with Whatman® glass microfiber filter paper drenched with 1 ml of 0.5 M H_2SO_4 acid, where atmospheric NH_3 diffuses to the acid. The concentration of NH_3 in the open end of the DST is assumed to be equivalent to NH_3 concentration in the air and zero towards the closed end creating a concentration gradient which allows obtaining the diffusive flux. DST for measuring NH_3 concentrations in air was required for measuring emissions of NH_3 from slurry storage ponds and fields receiving slurry applications. The samplers are usually arranged in towers capable of measuring the NH_3 concentration gradient above the source in conjunction with air mass flow rates. This enables the NH_3 flux from the source to be calculated.

3.5.2.2 Calibration of DSTs

i) Calibration against standard concentrations of "bagged" NH_3

The tubes were first standardised and calibrated in the laboratory for testing the adsorption capacity and efficiency using known concentrations of NH_4Cl and 1 M NaOH in 8 L GS-bags (Figure 3.12). NH_3 gas was generated in GS-bags by reacting NH_4Cl and 1 M NaOH in the GS-bags, which were left for one hour to attain equilibrium and then gas was transferred using a Syrman genia® 0.3 L syringe from the gas generation bag to gas collection bag, which contained the passive samplers (Figure 3.13). After exposing the tubes for 8h in the GS-bag, DSTs were extracted in 9 ml deionised water which was then analysed separately for trapped NH_4^+-N on the filter paper using colorimetric analysis.

Figure 3. 12: Generating NH_3 gas in 8 L GS-bags

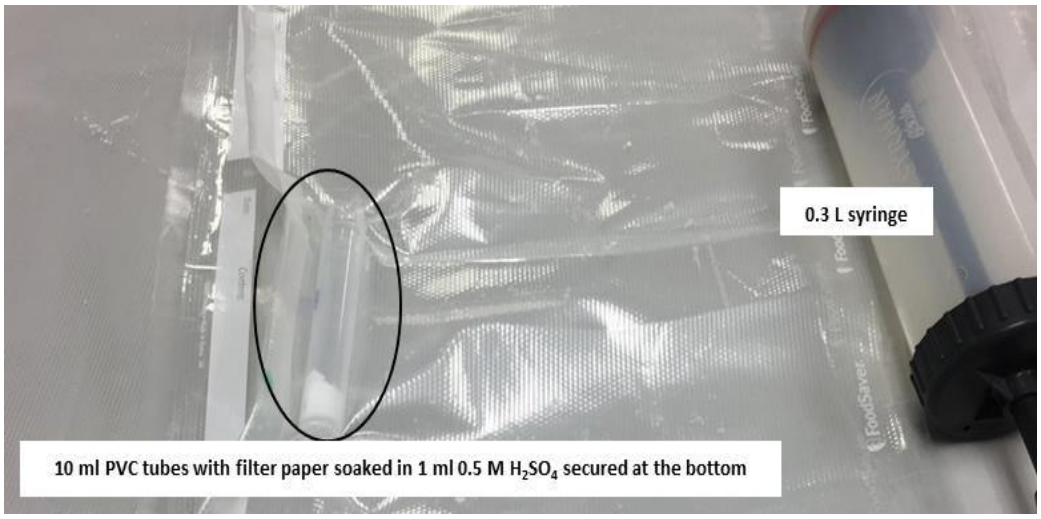


Figure 3. 13: Standardisation of DST in GS- bags

3.5.2.3 Results

A linear relationship was found between the NH_3 concentrations generated in a GS-bag and the amount of NH_3 loaded on to the filter paper in the tube DST (Figure 3.14). During 8 h when the tubes were placed in the bags less than 2% of the NH_3 in the 8 L bag was transferred to the filter paper in the sampling tube. This result also showed that the passive samplers needed calibration against an active sampling method capable of measuring the actual concentration of NH_3 in the air at the sampling site.

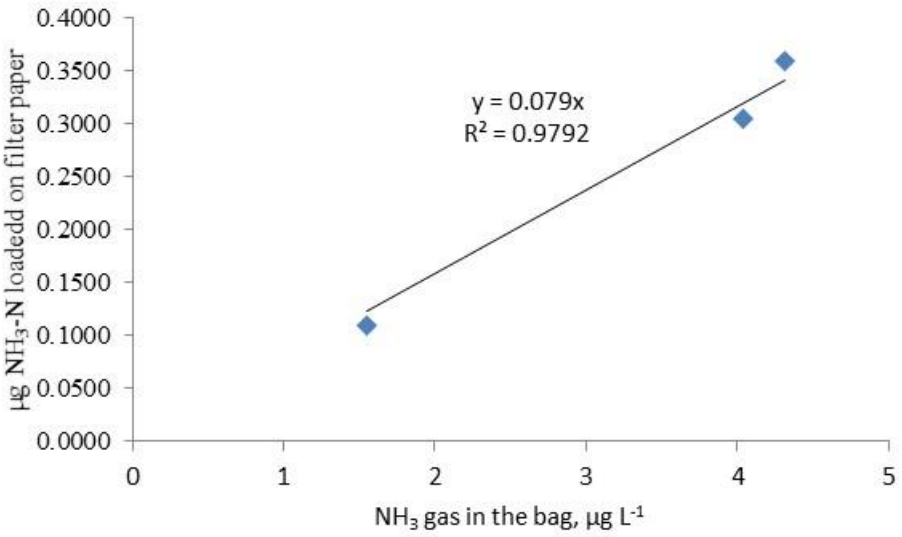


Figure 3. 14: The relationship between NH_3 loaded on filter paper (µg NH_3 $paper^{-1}$) secured at the bottom of passive flux sampling tubes and relatively high concentrations of NH_3 in the air (enclosed in the GS- bags).

ii) Calibration against active acid scrubbers

Since the passive samplers do not sample a defined volume of the air, they needed to be calibrated by knowing NH_3 concentrations in the air that were simultaneously measured by active acid scrubbers (section 3.4.3) as a reference method. The concentration of NH_3 in the air loaded on the filter paper in DSTs was obtained from the linear relationship between the NH_3 trapped by DST and NH_3 gas concentration in the air sampled by the active acid scrubber for exposed time period (24, 48, 72 and 96 h). The effective air flow rate was determined empirically by following equations

$$y = bx \qquad \text{(Eq. 3.2)}$$

where, y = slope and b = intercept of linear regression of the mass of NH_3 captured in the active acid scrubbers. Briefly, the linear regression slope was used as flow rate for DSTs (L min^{-1}) to calculate the NH_3 concentrations in the air. For each time period the sampling rate was calculated by using a conversion factor, for example the conversion factor for 48 hours was calculated using Eq. 3.3.

$$cf_{48} = \frac{m_{loaded\ on\ filter} * b}{time} \qquad \text{(Eq. 3.3)}$$

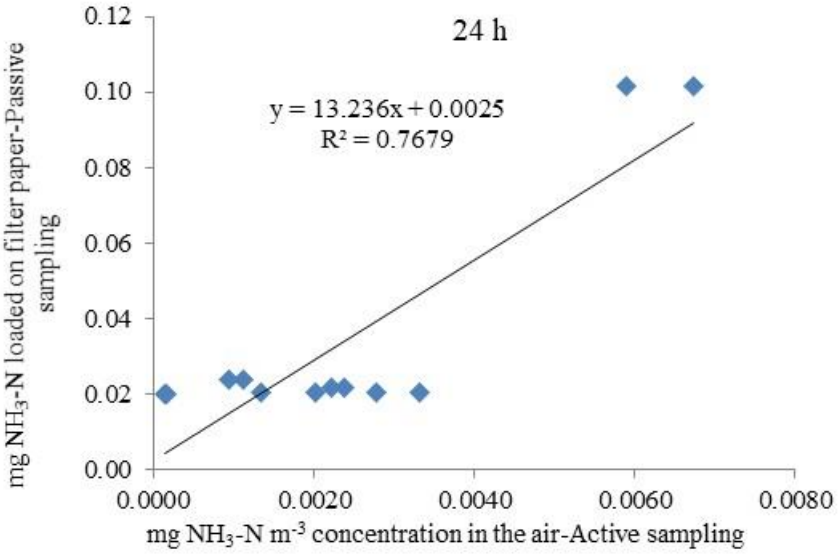


Figure 3. 15: Relationship between active NH_3 sampling in air and passive NH_3 sampling tubes placed on a vertical tower at downwind edge of the slurry storage pond for 24 h

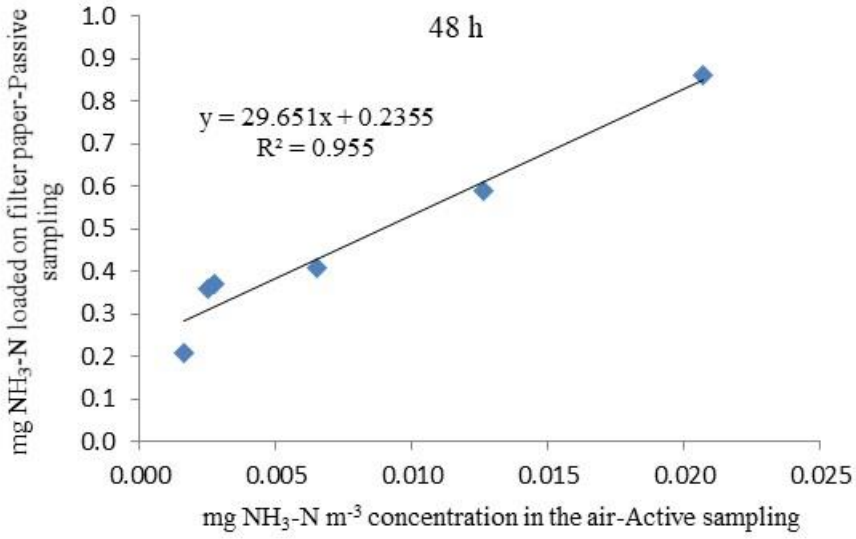


Figure 3. 16: Relationship between active NH_3 sampling in air and passive NH_3 sampling tubes placed on a vertical tower at downwind edge of the manure storage pond for 48 h

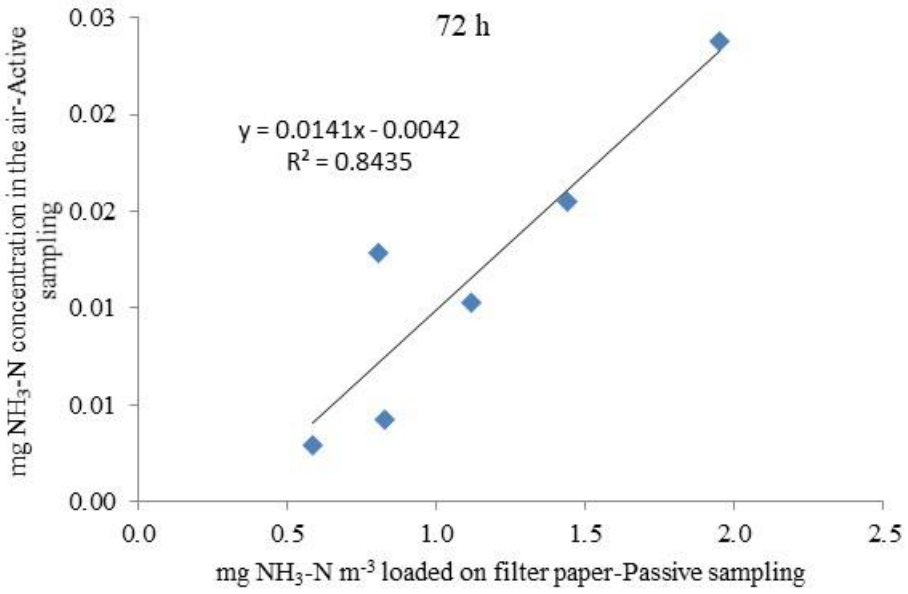


Figure 3. 17: Relationship between active NH_3 sampling in air and passive NH_3 sampling tubes placed on a vertical tower at downwind edge of the slurry storage pond for 72 h

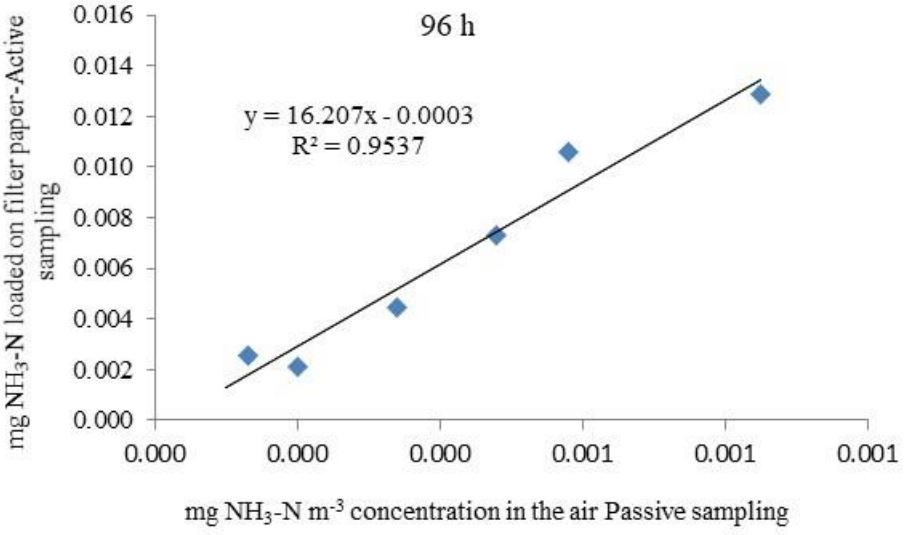


Figure 3. 18: Relationship between active NH_3 sampling in air and passive NH_3 sampling tubes placed on a vertical tower at downwind edge of the slurry storage pond for 96 h

Preliminary placement of active acid scrubbers and DST in the field above slurry pond indicated that the NH_3 concentrations in the air over 48 h would be in the range 0.02 to 0.101 mg NH_3-N m^{-3} for active sampling and 0.001 to 0.064 mg NH_3-N m^{-3} for passive sampling placed at downwind edge of the pond. Passive sampling techniques have been widely used (Sommer et al. 1996; Liu, Wang, and Beasley 2008; Puchalski et al. 2011) for measuring NH_3 emissions but our DST are not only simple and cost effective but also

easy to calibrate in the laboratory by simply using the GS-bags. Mostly wind tunnels (Puchalski et al. 2011) and expensive photo-acoustic infrared spectroscope (Wang et al. 2016) have been reported to be used for calibrating passive samplers in the literature.

3.5.2.4 Conclusions

The simplicity, cost, ease of deployment are advantages of using DST. A linear relationship was obtained for each time (24, 48, 72 and 96 h) and DST was found were useful for observing ambient concentrations of NH_3. This relationship enabled to continue the measurements without using active acid scrubbers and continue the measurements over a long time period (refer chap 6 and 7).

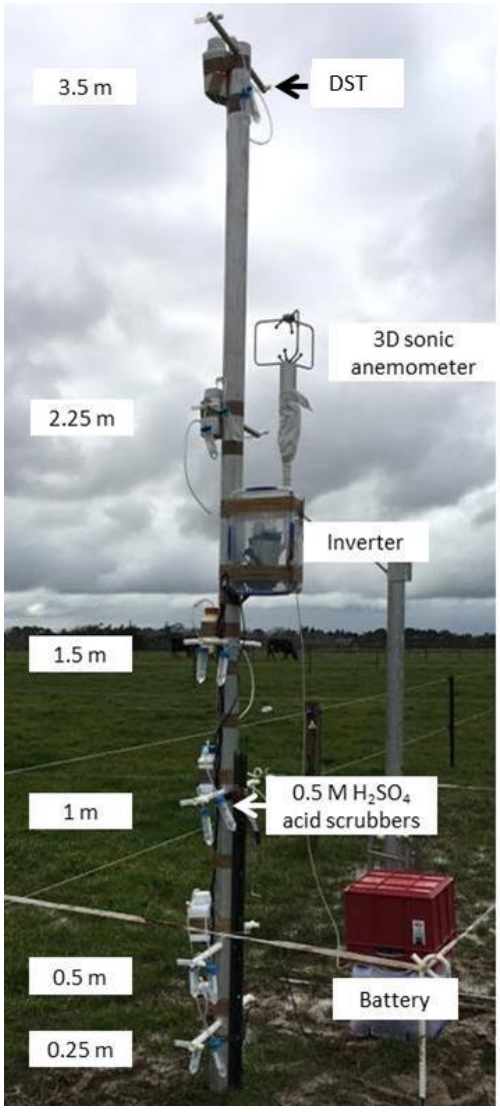


Figure 3. 19: Field set up showing active acid scrubbers and DST mounted at various heights to integrate horizontal flux coupled with 3D sonic anemometer to record wind speed and wind direction.

3.6 Efficiency of ammonia absorption and comparison of active and passive samplers

Different acid traps (oxalic, boric etc) have been used (Ndegwa et al. 2009; Wood, Marshall, and Cabrera 2000) for trapping NH_3 in the literature but we did not attempt to test the absorption efficiencies of different acids. In the field (storage pond measurements) 10 ml PVC DST were placed at various sampling heights along with the active acid scrubbers. Passive NH_3 sampling provides an opportunity to identify hot spots and estimate losses quantitatively because of its ability to quantify NH_3 was well established against ($R^2 = 0.87$) active samplers (Figure 3.16). The calibration of DSTs against active acid scrubbers enabled long term measurements of NH_3 emission from storage pond. For passive sampling as the concentration decreases the efficiency of NH_3 trapping drops off because the diffusion gradient decreases therefore the traps need to be calibrated with high and low NH_3 concentrations.

A comprehensive review of appropriate techniques for measuring NH_3 emissions at animal facilities has been presented by section 2.5 in chapter 2 of thesis. These include measuring the concentration of NH_3 gas absorbed in acid traps (wet chemistry) (Misselbrook et al. 2005b; Singh, 2007), passive samplers (Ferm tubes, impingers) (Tang, Cape, and Sutton 2001) and micro meteorological techniques (integrated horizontal flux, Eddy covariance) (Hu et al. 2014). All these methods have been developed, tested and used in closed ventilated or mechanically ventilated animal housing barns. However, for open or naturally ventilated system these methods require adaptations. Measuring NH_3 gas concentrations in naturally ventilated barns is challenging because of large volume of air flowing through the open ventilations (Ni and Heber 2008). The most extensively used methods for measuring NH_3 gas concentration are based on active or passive gas sampling. The active sampling captures NH_3 by flushing atmospheric air through an acid trap (tubes, bottles or denuders) with the help of an air pumps (McGinn and Janzen, 1998; Singh 2007; Hu et al. 2014). A passive sampler simply consists of a tube containing an acid (oxalic or phosphoric or sulphuric) or acid coated/impregnated glass filter paper to adsorb NH_3 gas by diffusion (Leuning et al. 1985; Puchalski et al. 2011). Measuring emissions from animal excreta deposited in naturally ventilated barns can be conducted either from the whole dairy cows' barn or from the multiple stages of management of the source (animals, excreta deposition on the floor, floor cleaning or scraping schedule)

separately and then adding them all together to obtain the whole system emission rate. Whole system NH_3 measurements suit situations where livestock are continuously housed and require information about the complete process, ventilation rate and airborne concentrations in the air (Ni et al. 2000). Nevertheless, it is important to note that measuring the ventilation rates in animal buildings, specifically naturally ventilated barns, is very challenging and is a main constraint to obtaining the NH_3 emission rate. Likewise, due to spatial and temporal variations in NH_3 emissions it is crucial to measure emissions from a number of locations to get accurate values of average concentrations. This is often impractical because of the high cost, time, sophisticated equipment and manpower required (Ni and Heber 2008). Therefore, from the wide range of available methods reviewed in Chapter 2 active and passive NH_3 sampling coupled with integrated horizontal flux measurements were chosen to quantify NH_3 volatilization losses from manure deposition on the barn floor, storage pond and manure re-application to land. The techniques reported in this chapter are well suited for deployment under laboratory and field conditions. Enclosure system has been widely used for quantifying NH_3 emissions mostly from land application of effluents in NZ (van der Weerden et al. 2014; Li et al. 2015). Only a few studies have reported using mass balance IHF methodology by simulating urine deposition grazed pastures (Laubach et al. 2013). We replaced the expensive shuttles with simple acid scrubbers and DSTs which are handy, cost effective, simple to evaluate and analyse in the lab for NH_3-N content. DSTs provide alternative and cheaper approach for quantifying NH_3 from various hot spots of manure management chain.

3.7 Summary and deployment of the techniques

Simple low cost samplers, simple acid bubblers, passive diffusion tubes have been produced and evaluated for measuring NH_3 emissions in the following situations. Passive samplers can be successfully used to monitor ambient NH_3 levels but these must be validated and calibrated against reference method (active acid scrubbers). All the techniques reported in this chapter are inexpensive compared to other techniques reported in the literature. These will allow NH_3 emissions to be quantified from all the stages of manure management without the need for more highly sophisticated and expensive laser attenuation instruments. The cow barn that is the focus of this study is an open sided naturally ventilated barn system which makes air flow measurement very challenging. A

time and motion study (Chapter 5) was therefore conducted on the deposition of urine and dung from the cow and the movement of slurry to the storage pond. This study showed that the period of NH_3 emission from mixed dung and urine was short and therefore NH_3 release from slurry could be simulated (ex-situ) using chamber techniques involving preserving jars. The chamber technique allowed for the challenges, cost and uncertainties associated measuring NH_3 loss from deposited slurry in naturally ventilated barns to be avoided. The experiments using the preserving jars as chambers are reported in Chapters 4 and 5 and the acid scrubbers and DSTs are reported in chapter 6, 7 and 8 of thesis.

3.8 Conclusions

The following major conclusions can be drawn from this chapter

- Static/dynamic chambers and preserving jars are well suited to quantify NH_3 emissions from sources that can be stored or simulated in these small enclosures.
- Replacing 7 L chambers with 1 L Agee preserving jars further simplifies the NH_3 measrement technique without employing compressed air.
- Both active and passive NH_3 sampling techniques were found useful for measuring NH_3 emissions from hotspots (urine and dung) and various surfaces in a barn, storage pond and paddocks).
- 8 L GS-bags are very useful to capture NH_3 gas from the source and to calibrate DSTs.
- DSTs are simple and cheap alternative to ferm tubes and shuttles.
- Modified IHF methodology allows long term measurement of NH_3 from the barn and storage pond.

Chapter 4

An investigation of the influence of urine-N concentrations on the ammonia emission flux from cow barn slurry mixtures.

4.1 Introduction

The expansion of dairy industry in New Zealand (NZ) involved both increased area of grazed pasture along with the increased use of feeding supplements e.g. maize and grass silage plus grains and palm kernel expeller meal (Christensen et al. 2012). Traditional pasture based grazing systems in NZ now include supplementary feeding infrastructures (feed-pads, Herd-Homes®, and cow barns). The use of feed-pads, Herd-Homes® and wintering barns requires manure storage and re-application to land (Houlbrooke et al. 2011; Livestock Improvement Corporation and DairyNZ 2017). Adopting supplementary feeding infrastructures has been very effective in reducing NO_3^--N leaching loss to water (Christensen et al. 2012; Doole 2015) , however there's very little information on gaseous N losses particularly NH_3 volatilization from these facilities. Where Herd-Homes® and barns have been used to specifically reduce N loss to water there is concern that the mitigation of one environmental problem has enhanced GHG losses from the dairy N cycle (Longhurst et al. 2006; Monaghan and de Klein 2014). Ammonia (NH_3) emissions from livestock farms have been a concern over the past few decades because of its negative effects on water and air quality (Hu et al. 2014).

NH_3 losses from cow barns in Europe (Ngwabie et al. 2009; Schiefler, 2013; Herbut and Angrecka, 2014; Mendes et al. 2015) and United States (Hristov et al. 2011; Todd et al. 2011) have been estimated in several studies that were reviewed in Chapter 2. In NZ, NH_3 losses from the hybrid dairy systems involving grazing and periodic housing of cows have not been quantified (Laubach et al. 2015; van der Weerden, Luo, and Dexter 2014). Dairy cattle excreta deposited on concrete barn floor of a free-stall barn is mixture of urine and dung only. This slurry is scraped to a channel located underneath the barn floor where it may take 3 - 7 days to move by gravity to a storage pond, where slurry can be stored for up-to 3 months before re-application to land. Many freestall barns have automatic excreta

scrapers operating (every 2 hours) in the laneways which scrape the excreta collected in a cow yard to the storage channel to keep the facility clean.

It is well known that if dairy cows are fed protein rich diets then the urea content of the excreta N can be raised as the cow excretes surplus N as urea in the urine stream (Kebreab et al. 2002; Kyamanywa et al. 2020). Under these circumstances TAN concentrations on the manure can be expected to rise rapidly perhaps leading to greater NH_3 volatilization. This study investigates the effect of urinary–N concentration on NH_3 emissions rate from dung and urine slurries simulating those created in a free-stall barn. The review of the process of NH_3 formation, release and dispersion from dairy manure has been presented in Chapter 2 section 2.3. Theory suggests that the initial urea concentration of the slurry will have greatest influence on the initial pH and NH_4^+ concentrations of combined urine dung slurry mixtures. Therefore the hypothesis of the experimental work is "the flux of NH_3 gas emission from a slurry mixture can be predicted based on the urea content of urine and pH of the slurry at constant temperature". A better understanding of the factors stimulating NH_3 volatilization from dairy cattle manure and subsequent stages of manure management will help develop mitigation strategies to minimise the emissions from hotspots within manure handling systems.

4.2 Materials and Methods

4.2.1 Urine and Dung Samples

The current study derived urine and dung from a dietary trial (Kyamanywa et al. 2020) designed to evaluate the urinary load from dairy cows partially housed in late summer-autumn and partially grazed on pasture, supplemented with summer crops and silages. Bulk urine samples were collected separately from 3 groups of dairy cows in the dietary trial, each group containing 18 cows (total 54). Cows in each respective group were fed high crude protein (HCP), medium crude protein (MCP) and low crude protein (LCP) diet, respectively as given in Table 4.1.The naturally generated urines had a range of urea-N concentrations (~1000 mg L^{-1} to ~6000 mg L^{-1}), collected from dairy cows fed on three crude protein levels. Dung samples were recovered from dung patchs deposited on clean collecting yard surfaces and bulked into one single sample. These urine and dung samples were used to create urine and dung slurries with a range of initial urea-N concentrations.

Table 4. 1:The diet fed to the cows for the collection of urine and dung for the in vitro measurements of NH_3 gas (Kyamanywa et al. 2020)

Treatment	Feeds	Average CP content %
HCP	Ryegrass (*Lolium perenne* L.)	25
MCP	Mix hunter leafy turnip (*Brassica campestris* ssp. *rapa*), pasture silage and maize silage	18.5
LCP	Mix of hunter leafy turnip and supplements	13.5

4.2.2 Chemical Analysis

Triplicate sub samples (pseudo-replicates) of the dung and slurry mixture were analysed fresh, and dry matter (DM) content determined by drying to constant weight at 105 $^{\circ}$C in drying oven overnight. Urine samples were analysed for urea N content by reacting with diacetyl monoxime and thiosemicarbazide in acid conditions and reading the absorbance at 520 nm (Mulvaney and Bremner 1979). The total Kjeldahl N and P (TKN and TKP) in fresh (wet) urine, dung and slurry mixture was determined using a Technicon auto analyser after digesting 1 g (w/v) of sample with 4 ml of Kjeldahl digest acid at 360 $^{\circ}$C for 4 hours (McKenzie, H.K and Wallace 1954). The C:N ratio in dried dung samples was obtained by combustion in a TruSpec (LECO Corp. St. Joseph, MI, USA) CHNS analyser (Matejovic 1993). Mineral N (NH_4^+ and NO_3^-) content of the urine (5 ml urine), dung (5 g) and slurry mixture (5 g) was measured by extracting the samples with 2 M KCl with 25 ml of 2 M KCl followed by shaking, centrifugation and filtration through Whatman 42 filter paper) and analysing the NH_4^+ concentration in the sample by colorimetric analysis (Blakemore et al. 1987). The KCl extraction provided the total ammoniacal nitrogen values (TAN) for slurry mixtures sampled during the incubation and used in the prediction of NH_3 emissions by the Chaoui et al. (2009) model section 4.5.2. Urine, dung and slurry pH was measured by using a Thermo Orion Star™ A214 bench top pH meter in the laboratory. The urine, dung and slurry pH was measured at time zero just before sealing the preserving jars and then every two hours for the first eight hours followed by every 24 hours.

4.2.3 Ammonia gas emission measurements

NH_3 emissions from the first 5 slurry mixtures (403 – 2454 mg urea-N L^{-1} slurry, Table 4.3) were measured in vitro in a laboratory set up at room temperature (18 $^{\circ}$C - 24 $^{\circ}$C) for 6 days. The laboratory set up consisted of Agee jars (1 L preserving jars) with passive acid traps (10 ml 0.5 M H_2SO_4) contained in 50 ml poly vinyl carbonate vials supported by laminating sheets (with holes) placed in slanting position over the slurry mixture (Figure 4.1). The slurry mixture was reconstituted to represent a standard rate of excretion by dairy cows (Haynes and Williams 1993) at a ratio of 1 : 1.3 (dung : urine) by mixing freshly collected urine and dung [(w/v); wet basis] in 100 ml poly vinyl carbonate urine containers. Then the homogenised slurry mixture was immediately transferred from urine container to 50 ml poly vinyl carbonate vials to be incubated in preserving jars. Three replicate jars were prepared for each concentration of urea. The NH_3 gas released from the slurry mixture is transferred from the source to the acid trap by diffusion. Acid traps were changed every 24 hours and the measurements continued for 144 hours (6 days). In this study acid traps were changed every 24 hours to simulate the effect of slurry remaining on a surface for upto 6 days. Aliquots of the trapping solution were taken for analysis of NH_4^+-N by (colorimetric analysis) auto analyser. The emission rate of NH_3 was calculated based on following equation

$$F = \frac{XV}{At} \qquad \text{(Eq.4.1)}$$

where X is the concentration of NH_3-N in the acid trap (mg L^{-1}), V is the volume of the acid (L), A is the exposed surface area (0.005 m^2) and t is the duration of the measurements (h). It is important to maintain that NH_3 emissions were corrected using the relationships for NH_3 recovery presented in Figure 3.10 (a,b) Chapter 3.

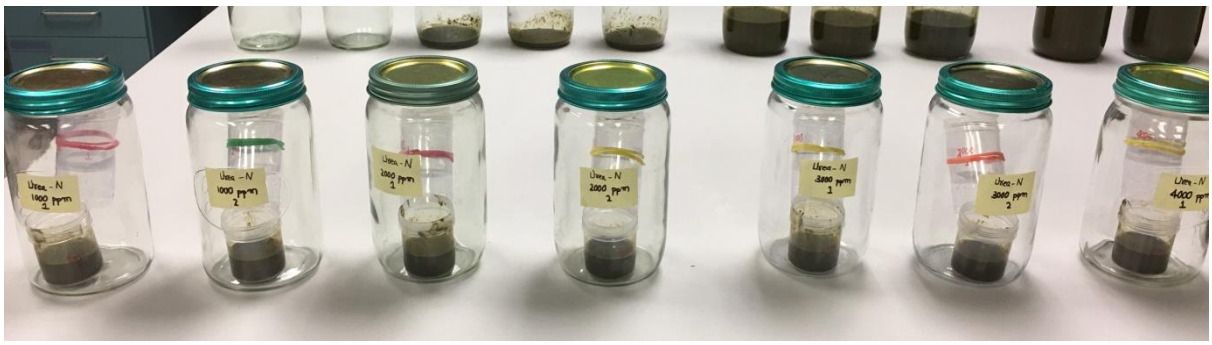


Figure 4. 1: Laboratory set up for measuring NH_3 emission flux from slurry mixture

4.3 Regression analysis

Relationships between the NH_3 emission flux measured during the experiments and different driving parameters (e.g pH of slurry) were developed and observed using least squares regression analysis. The regression equations and empirical modelling (based on experimental observations between two or more parameters) were performed using Microsoft Excel 2013.

4.4 Results and Discussion

4.4.1 Trends in pH of urine, dung and slurry

The composition and chemical analysis of the dung (Table 4.2) and urine (Table 4.3) samples used to form the dung and urine slurries used in this experiment created slurries with a wide range (403 – 2918 mg urea-N L^{-1} of urinary urea) and total N concentrations (2917 – 5387 TKN mg L^{-1}, Table 4.4). The total N in the slurry mixtures increased consistently with the increase in urinary urea and similar trend was observed in pH of the individual urine samples and slurry mixtures (Table 4.3 and 4.4). The effect of lowering diet crude protein will be discussed in next chapter, here we mostly emphasize on relationship between urinary urea and pH on diffusive NH_3 flux.

Table 4. 2: Chemical composition of the dung used for the experiment

Parameters	Dung
pH	6.67(0.02) [a]
Dry Matter (%)	11.2 (0.03)
TAN[b] (mg L^{-1})	--
Total N (mg L^{-1})	3408 (86.9)[a]
Total P (mg L^{-1})	12.50(0.18) [a]
C:N	21

a Values expressed on fresh weight basis of fresh samples collected off the one slurry mixture

b TAN= Total ammoniacal N

values in parenthesis represent standard error (SE) of the mean (n=3)

Table 4. 3:The measured urinary urea-N concentration in urine and slurry mixture at time 0

Measured urinary urea-N mg L^{-1}	Measured urea-N in slurry mg L^{-1}
714 (4.13)*	403.13
2792 (4.34)	1581.54
3469 (35.38)*	1954.42
4057 (17.30)*	2291.94
4330 (7.52)*	2454.27
5158 (13.44)*	2918.77

*values in parenthesis represent standard error (SE) of the mean (n=3)

4.4.2 Measured NH_3 emission loss

The total N losses through NH_3 emissions (expressed as %TKN added, Table 4.4) were low (< 11%) possibly because of acid production from dung fermentation causing pH to fall and hence limiting the process of volatilization by 144 h (Figure 4.2). When cumulative NH_3 emissions were expressed as % of total urea N applied 17 to 47% was volatilised and the rest presumably remained as NH_{3aq} in the solution or was immobilised through reactions with dung. However, the dung has a low C:N ratio (21, Table 4.2) and is unlikely to stimulate immobilization of inorganic N into organically bound N reducing the availability of free TAN.

Table 4. 4: The urea-N concentrations in 23 g of mixed urine-dung slurry and amount of total N added to the incubation jars and %N volatilized and captured in the passive acid traps

Urea-N mg L^{-1}	Concentration of slurry TKN mg L^{-1}	Total TKN added mg	Total N volatilised %
403.13	2917.83	67.11	6.57 (0.49)*
1581.54	3953.87	90.93	6.69 (0.67)*
1954.42	3440.09	79.12	9.91 (0.86)*
2291.94	4321.83	99.40	8.95 (1.00)*
2454.27	4914.17	113.02	9.70 (1.26)*
2918.77	5387.26	123.90	10.9 (1.60)*

*values in parenthesis represent standard error (SE) of the mean (n=3)

The effect of various urinary N levels on NH_3 emission flux from slurry mixtures over 6 days (24 h to 144 h) is shown in Figure 4.2. As the initial urea-N concentration of the urine-dung slurries increased pH and NH_3 emission flux also increased. There was a curvilinear increase in NH_3 emission flux that could be fitted with an exponential relationship. The highest rate of NH_3 emissions flux for all urea concentrations occurred in the first 24 h and 48 h followed by lower flux from 72 h to 144 h. The higher flux rates are consistent with the highest slurry pHs being recorded in the first 24 hours (Figure 4.3). Typically NH_3 emission flux from dairy cattle urine applied to soil has been characterised by high emission flux in the beginning reaching the background level with passage of time (Amon et al. 2006; Laubach et al. 2013).

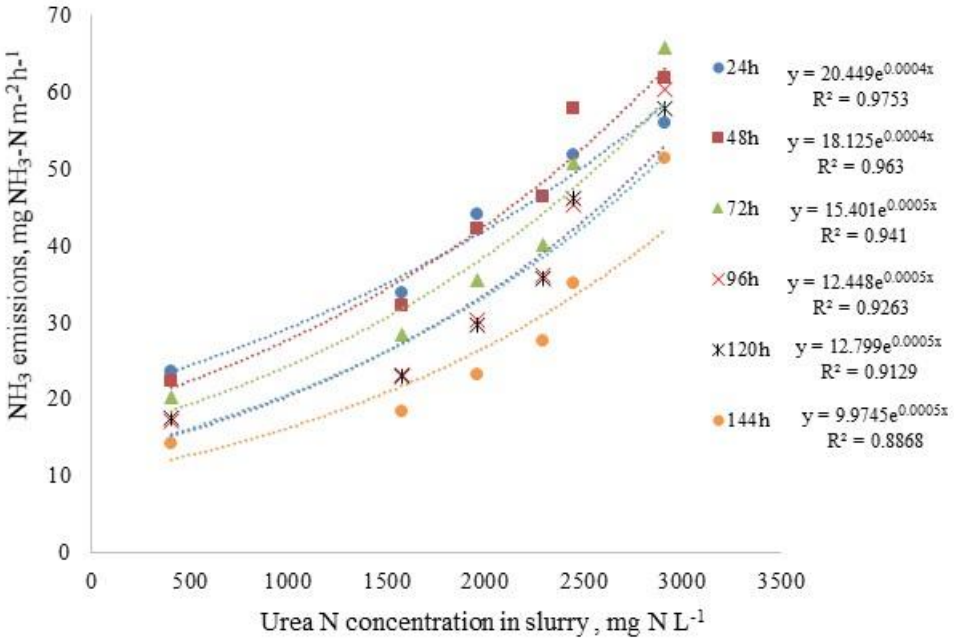


Figure 4. 2: NH_3 emission flux at 6 time intervals (24 – 144 h) during the incubation (18 ºC - 24 ºC) of slurry with 5 different initial urea concentrations, created using urine from dairy cows fed diets of different crude protein content.

It has been reported that most NH_3 volatilization takes place in the first 24 hours following the excretion of manure because rate of urea hydrolysis is a function of urea concentration in the urine (Muck and Steenhuis 1982). The urea concentration is high soon after the urine excretion leading to rapid urea hydrolysis which causes initial build-up of aqueous NH_3 in the urine and a high initial rise in pH causing higher NH_3 emission flux (Muck and Steenhuis 1982). NH_3 emissions are driven by the hydrolysis of urea in the urine component along with minor contribution from other organic N constituents of urine

whereas emissions from dung are considered negligible (Pereira et al. 2012). For example, the initial pH (first 10 hours of incubation) of dung alone is significantly lower than urine alone (Figure 4.3a).

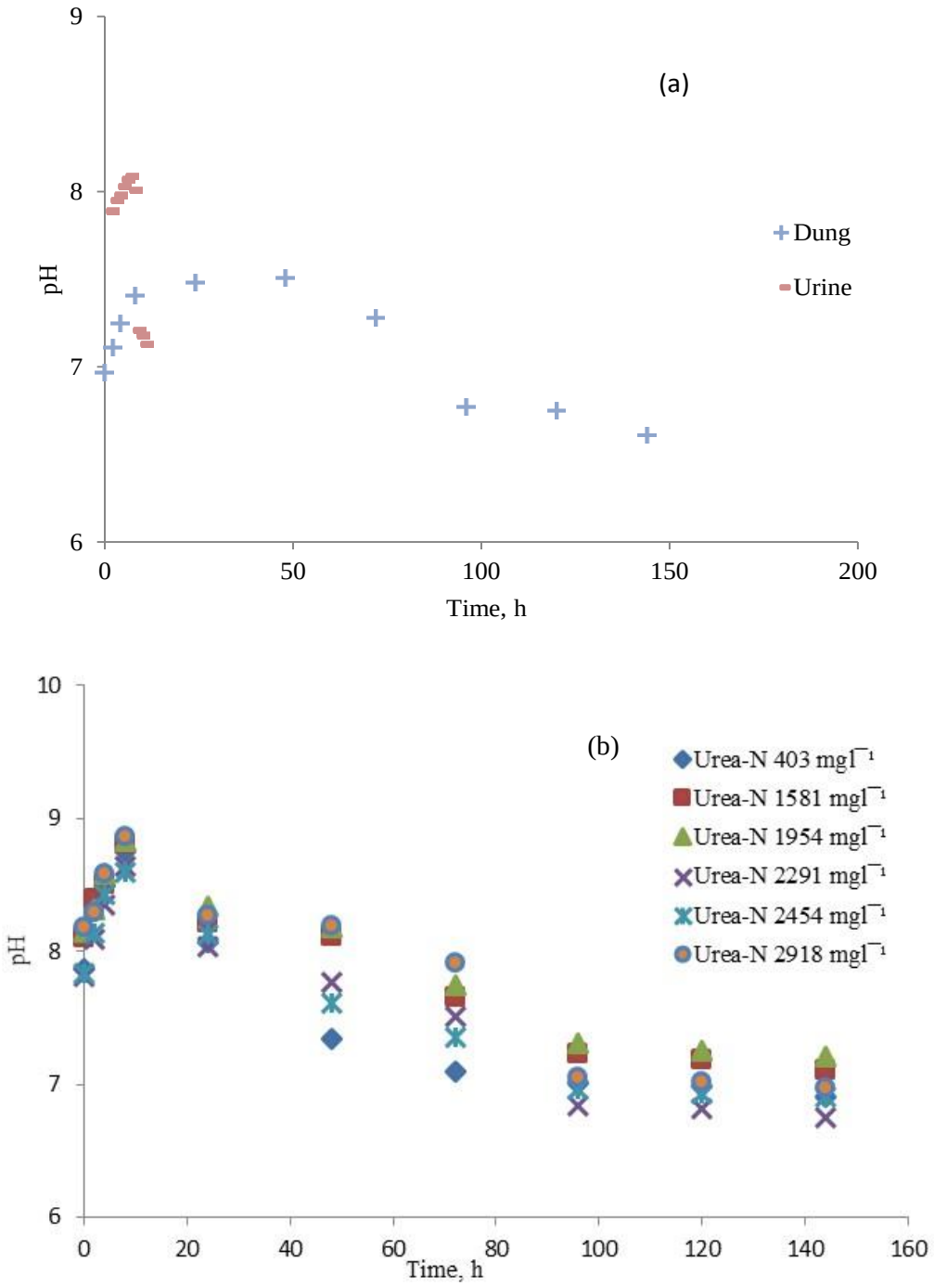


Figure 4. 3: a) The pH of urine and dung samples and (b) and of slurry mixture during the incubation at 18 ºC - 24 ºC in a closed system with different initial urea-N concentrations

The pH values averaged from ~6.9 to 8.17 in all the slurry mixtures over 6 days (Figure 4.3 and Figure 4.5). The initial high pH is consistent with hydrolysis of urea and is related

to the initial urea-N concentration in the slurry (Figure 4.2). Initial pH is rapidly elevated by the mixing of urine and dung but with the passage of time pH of the slurry decreases. The slurry pH increased steadily over the first 24 h particularly in first 16 h because of the hydrolysis of urea and dissociation of ammonium carbonate $(NH_4)_2CO_3$ and release of carbon dioxide (CO_2) gas. CO_2 gas (generated from decomposition (respiration) of the dung) is present at the aerobic surface of the slurry raising the concentration of carbonic acid, which would moderate the pH increase. The degradation and mineralization of dung can also be an important factor influencing the pH of the slurry. Notably the pH of the dung alone also increases during the first 24 h after deposition (Figure 4.3a) before declining over time. On average there is a strong negative linear relationship between time and the pH of the slurry (Figure 4.5).

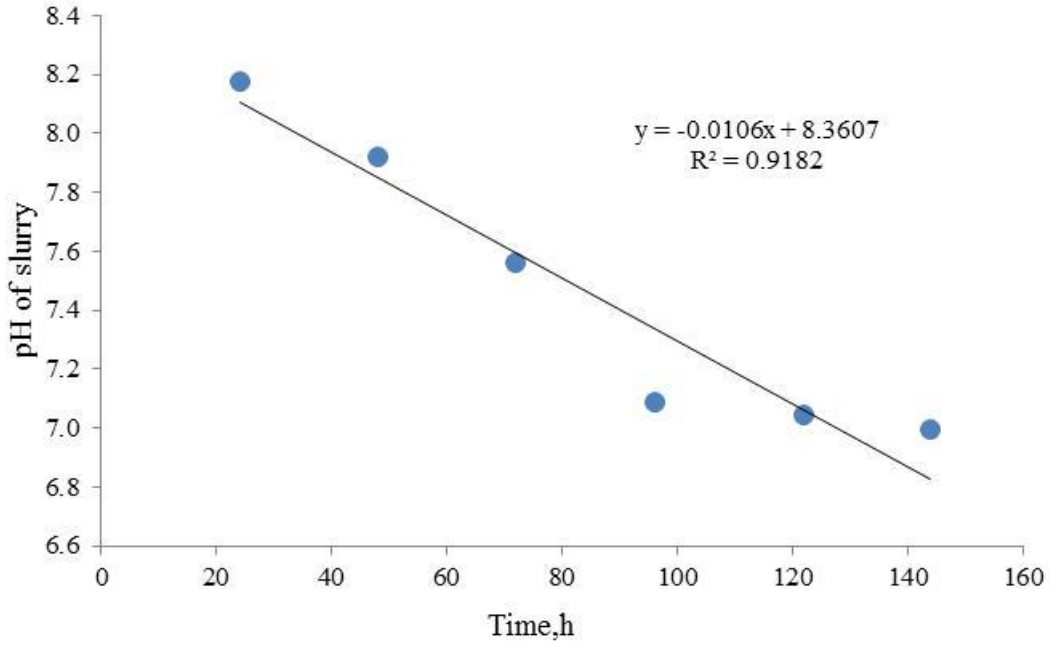


Figure 4. 4: Relationship between pH of slurry (averaged across all initial urea-N concentrations) and time over 144 h

In cattle slurry NH_3 concentration, pH and temperature affect the equilibrium vapour pressure above the surface (Muck and Steenhuis 1982), whereas in the present study TAN and pH of slurry were main factors inducing NH_3 emissions because the temperature was kept constant.

The high pH of the urine and dung slurry results from the high urease enzyme activity in the slurry mixtures providing ideal conditions for NH_3 formation and volatilization. The pH continued to rise for 48 h and then started to decline; this trend in pH was consistent

with trends in NH_3 volatilization flux (Figure 4.2). The emissions and pH peaked at the same time (8 - 24 hours) higher emissions peaks were associated with higher initial urea concentrations and higher pH values. It is very clear that the pH of all slurries declines over time (Figure 4.5), which is consistent with the decline in NH_3 volatilization flux with time (Figure 4.2). The rate constants from the curvilinear relationships fitted to explain the influence of initial urea concentration on NH_3 emission flux (Figure 4.2) were plotted against the time averaged pH for each slurry mixture and illustrate a very strong positive relationship between pH and K the NH_3 emission rate constant.

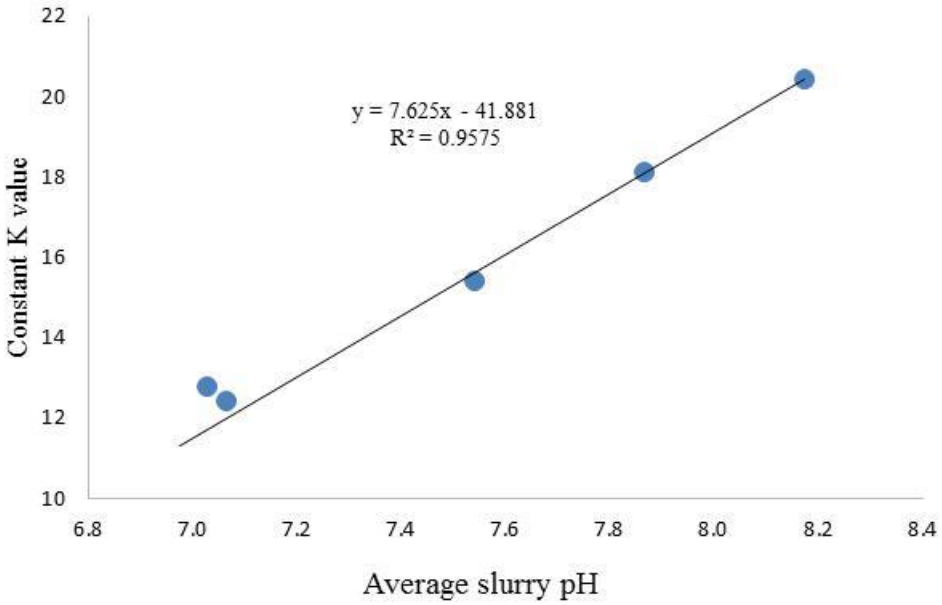


Figure 4. 5: Relationship between the NH_3 flux constant K values (Eq. 4.6) and pH of slurry (averaged across all incubation time, 144 h)

4.4.3 The Volatile ammonia fraction and emissions

Generally, at constant temperature, the proportion of unionized aqueous NH_3 in the TAN is directly proportional to NH_3 volatilization (Hartung and Phillips 1994). Likewise, at constant temperature NH_3 volatilization is the function of NH_{3aq} in the total TAN hence pH will determine the equilibrium between NH_4^+ and NH_3. Low pH favours the formation of NH_4^+ hence lowers the potential of NH_3 volatilization which is key factor in reducing NH_3 emission from dairy cattle excreta. Others have also shown that urine and slurry pH plays a key role in controlling volatilization of NH_3 and minute change in pH could have large impact on emissions (Sommer and Husted 1995). Using the trend in pH and initial TAN concentrations in the slurry mixtures a relationship between NH_3 emission flux and

pH was developed based on the model (Eq. 4.2) by (Chaoui et al. 2009). Chaoui et al. (2009), used the model by (Hashimoto and Ludington 1971) for predicting the un-dissociated fraction of NH_3 in solution (f) and the gaseous NH_3 fraction from the surface of manure using Henry's law constant (K_h)

$$f = \frac{NH_{3l}}{NH_4^+ + NH_{3_l}} = \frac{1}{1 + \frac{10^{-pH}}{0.81\ x\ 10^{-10} x 1.07^{(T-293)}}} \qquad \text{(Eq. 4.2)}$$

where, l represents the liquid phase, pH is the measured pH and T is the absolute temperature (K) whereas the ratio between NH_{3l} and NH_{3g} was estimated by converting Henry's constant to dimensionless form [kg NH_3-N $m^{-3}]_l$/[kg NH_3-N $m^{-3}]_g$

$$K_h = \frac{NH_{3_{(solution)}}}{NH_{3_{(gas)}}} = 1384\ x\ 1.053^{(293-T)} \qquad \text{(Eq. 4.3)}$$

After mixing urine and dung, the pH increased rapidly (Figure 4.3b) and also the NH_3 emission flux (Figure 4.2) but after 48 hours the trend in NH_3 emission slowed probably because of the decreasing pH and being limited by the diffusive mass transfer of the gas through the surface of slurry. This pattern of NH_3 emission did not appear to follow the model of Chaoui et al. (2009) and this is examined in the next section.

4.4.4 Comparison between predicted and measured ammonia emissions

The NH_3 emission chemistry discussed in Chapter 2; section 2.3 shows that initial urea concentration of the slurry will have greatest influence on the initial pH and NH_4^+ concentrations of combined urine dung slurry mixtures. Based on NH_3 emission chemistry and the relationships described by Chaoui et al. (2009) the predicted flux was calculated using Eq.4.4

$$J_{NH_3} = \frac{D}{X}\left[\frac{TAN}{(1 + 10^{(pKa-pH)})}/Kh\right] \qquad \text{(Eq. 4.4)}$$

where J_{NH_3} is the flux of NH_3 volatilization (mg NH_3-N m^{-2} h^{-1}), D is diffusivity constant (0.0000209 m^2 h^{-1}), X is distance between the manure surface and acid trap (m), TAN is total ammoniacal N (mg L^{-1}) and *Kh* is Henry's constant. The gas concentration at the surface of manure was determined based on the Eq. 2.8 (Chapter 2 section 2.3) and then Henry's law was used to estimate vapour pressure above the manure surface.

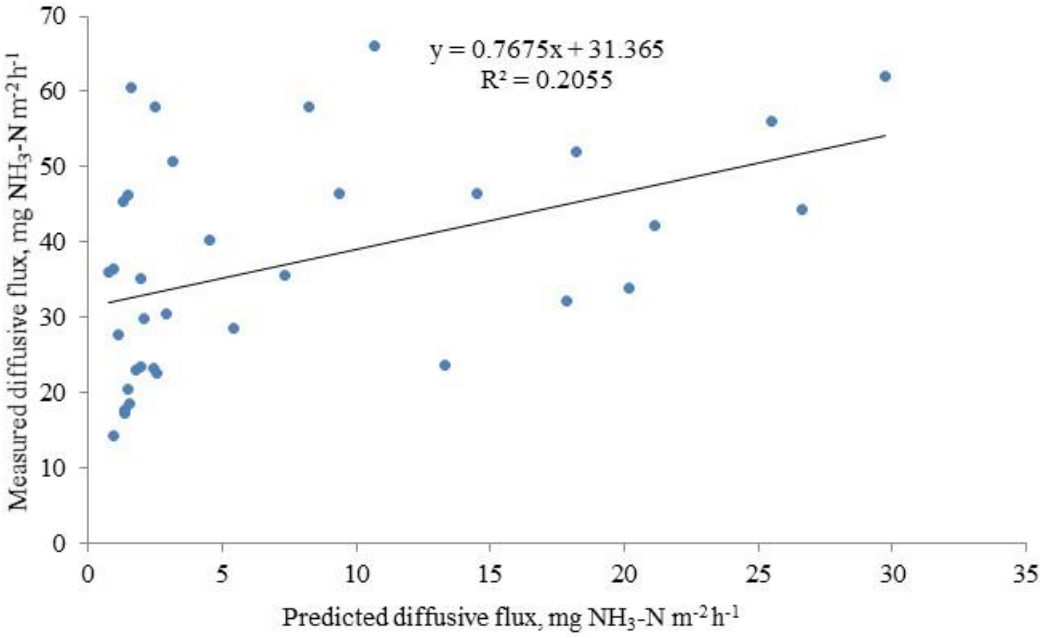


Figure 4. 6: Relationship between measured and predicted NH_3 diffusive flux based on the model by (Chaoui et al. 2009)

However applying the relationships described by (Chaoui et al. 2009) to the measured variables, the series of equations (Eq. 4.2 - 4.4) were unable to predict the relationship (R^2= 0.2055) between the predicted NH_3 emission diffusive flux and the measured values (Figure 4.6).

An alternative approach is to use the empirical relationships derived from Figure 4.2 (Eq. 4.5), the least squares regression best fits for relationships between NH_3 emission flux and initial urea-N concentrations in the slurry and Figure 4.7 and (Eq. 4.6), the relationship between the emissions rate constant and the average pH of the slurry.

NH_3 emission flux (mg N m^{-2} h^{-1})

$$= K_1 e^{k2(initial\ urea-N\ concentration)} \quad \text{(Eq. 4.5)}$$

and K_2 can be approximated as 0.0005 (mg N L^{-1})

$$K_1(m^2h^{-1}) = 7.625pH - 41.881 \quad \text{(Eq. 4.6)}$$

Using the initial urea-N concentrations in the slurry and the measured pHs of the slurries, Eq. 4.5 and Eq. 4.6 were used to produce predicted NH_3 emission flux (mg N m^{-2} h^{-1}), which are plotted against the measured NH_3 emission flux in Figure 4.7.

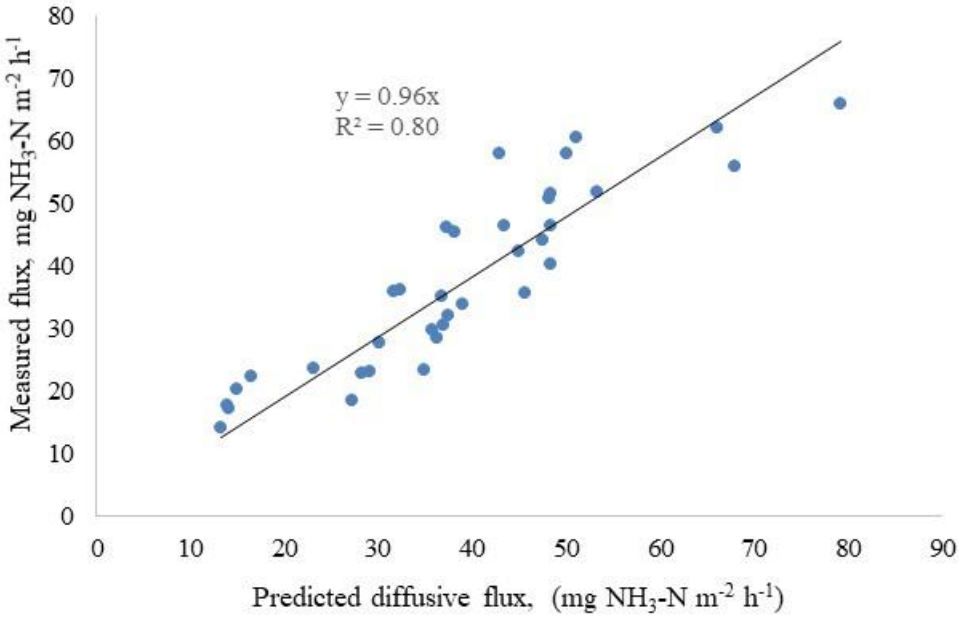


Figure 4. 7: Relationship between measured and predicted NH_3 emission flux (at each sampling time for all urea-N concentrations)

This combined model was used to predict the NH_3 flux from urine and dung slurries at all times during 6 days of incubation. This model explained 80% of the variation in the measured values (Figure 4.7). The relationship supported the hypothesis that "the flux of NH_3 gas emission from a slurry mixture can be predicted based on the urea content of urine and pH of the slurry at constant temperature" and urea concentration of the urine plays a key role in promoting NH_3 emissions.

4.5 General Discussion

NH_3 emissions are driven by various manure characteristics (pH, TAN, total N) and environmental factors (temperature, wind speed, relative humidity). In this laboratory incubation study, NH_3 emissions were solely dependent on manure characteristics specifically pH, urea and TAN content of the slurry mixtures. Various concentrations of urinary urea N ranging from ~700 to 5500 mg N L^{-1} were generated by increasing the dietary crude protein intake by dairy cows. Emissions of NH_3 contributed to total slurry N losses of less than 11% but the extent of emissions were strongly associated with the initial urea-N concentration in the slurry. The different urea-N concentrations in the urine used to form the slurries were derived from feeding dairy cows different levels of crude protein in their diet. Process based simulation models have been identified as one of the most economic options for estimating and evaluating NH_3 emissions from animal feeding operations (Monteny 2000). In some simulation models, NH_3 volatilization from the manure surface is predicted from four primary components: 1) the rate at which total ammoniacal nitrogen (TAN= NH_4^+-N and NH_3-N) is formed from manure due to urea hydrolysis 2) the rate of transport of TAN from the manure to the surface 3) the fraction of TAN available for volatilization 4) the rate of volatilization from the manure to atmosphere (Chaoui et al. 2009; Montes et al. 2008). Most of the studies have modelled NH_3 emissions from manure surface based on convective mass transfer. Quantifying N losses particularly NH_3 volatilization from an intensive grazing system including housing system is not only expensive but also challenging. NH_3 losses begin with N excretion in the form of urea in urine on the barn floor and laneway inside the barn or outdoor collection areas (milking shed, manure stores or the paddocks). Urease enzyme present in dung promotes urinary urea hydrolysis, slurry pH increases and NH_3 volatilization occurs (Ngwabie et al. 2009; Todd et al. 2008). In mixed dairy manure, nitrogen (N) exists as both organic and inorganic (Total ammoniacal, TAN). Total ammoniacal nitrogen is the sum of ammonium ion (NH_4^+) and unionized NH_3, generally the volatilization of NH_3 gas from any manure management stage is dependent on the concentration of free NH_3 in the liquid phase, which dictates the dissociated concentration of NH_4^+ ions. The excreted N is transformed into (TAN = [NH_3] + [NH_4^+]) or organic N by the process of mineralization or immobilisation, depending on the C : N ratio of the mixed excreta/manure (Sommer et al. 2006).

Ammonia emissions data obtained from a particular stage or hotspot from a manure management system cannot to generalised because of the number of management,

environmental and manure characteristics driving the emissions from a particular stage (Ni and Heber 2008; Shah et al. 2006; Hristov et al. 2013).

Overall the emissions of NH_3 from slurry follows the trends observed in the experiments of by Canh et al. (1998) on pigs, and Misselbrook et al. (2005d) and Pereira et al. (2012) on dairy cows, who also found that reducing the dietary N intake influenced the pH of the urine which influenced NH_3 emissions from excreta. The greatest source of NH_3 emissions are likely to be from the urine N content of the slurry and emissions from dung are considered negligible (Kellems, Miner, and Church 1979) (further explored in next chapter).

4.6 Implications of the study

The empirical model developed in this research is very useful for predicting the NH_3 emission from fresh slurry deposited on concrete laneways in free-stall barns. The fresh slurry remains there for up-to 2 h before a scraper transfers the slurry to a channel where gravity flow feed slurry to a storage pond. Over a period of 2 - 5 days (up to 144 h) the slurry moves through the channel to the pond. The results presented here suggests that 1% of NH_3 loss will occur in the first 2 h and a further 5 - 8% may be lost in the channel (delivering slurry to a storage pond), depending on the initial urea-N concentration in the slurry. Measuring NH_3 loss from slurry chambers does not simulate NH_3 loss from the aged slurry in the channel nor the open storage pond where slurry combines with rainfall. Emissions from the channel of the Massey No.4 Dairy Farm, free-stall barn and aged slurry material recovered from the channel are presented in Chapter 6. Emissions from the storage pond surface measured ex-situ in Chapter 7 were carried out over a longer period of time. Therefore the in vitro measurements made in this chapter, relate only to the first 0 - 2 h of the real scenario in a scraped free-stall barn where fresh slurry is being deposited every 2 h in the storage channel.

4.7 Conclusions

The above results confirm that NH_3 emissions from fresh dairy cow slurry are positively related to the initial urea concentration of the urine component of the slurry. This finding is supported by studies of Misselbrook et al. (2005d) and Pereira et al. (2012) who found that higher urinary urea concentrations in mixed slurries raised total ammoniacal N

concentrations and increased NH_3 emission loss in proportion to urine N content. This study was carried out with urine of variable urea N concentrations mixed with the same standard dung sample. In practice both urine and dung characteristics will change in response to changes in cow diet. The relationship between variable urea N and dung N on NH_3 emission flux from simulated barn slurry is researched in the next chapter.

Chapter 5

Effect of manipulating dietary crude protein intake by dairy cows on ammonia emissions: Laboratory incubation studies

5.1 Introduction

Results presented in Chapter 4, confirm that ammonia (NH_3) gas emissions from fresh dairy cow slurry are positively related to the initial urea concentration of the urine component of the slurry. This finding is supported by studies of Misselbrook et al. (2005d) and Pereira et al. (2012), who found that higher urinary urea concentrations in mixed slurries raised total ammoniacal N concentrations and increased NH_3 emission loss. These authors and others (Castillo et al. 2000; Todd et al. 2006; Powell et al. 2008; Totty et al. 2013;) have shown that the daily crude protein content of a cows diet strongly influences the partitioning of N between urinary N urea, dung N and milk N. Dairy cows are inefficient N users as they retain only 5 - 10% of feed N in milk and meat whilst 85 - 90 % is excreted back in urine and dung. The proportion of urea N in urine is highly dependent on the dietary crude protein intake (Castillo et al. 2000; Kebreab et al. 2001). High urinary N loads lead to greater N losses via NH_3 volatilisation plus increased N_2O emissions and leaching of NO_3-N from urine patches deposited when cows are at pasture (Selbie et al. 2015). NZ dairy farming is traditionally grazed pasture based (rye grass and white clover pastures) because of the low capital costs involved and favourable temperate climate compared to other farming systems, where cattle are kept in confinements and fed on supplementary diets. Ryegrass (*L. perenne*) and white clover (*T. repens*) pastures commonly offer a high crude protein diet (Litherland and Lambert 2007) and create high urinary loads in grazed pasture systems. In rain fed climates dry periods decrease pasture growth and then it is common to supplement the cow's diets with stored grass silage, imported maize silage, or, a crop grown specifically to enhance the feed supply and feed quality (e.g. summer brassica crops). Recently Kyamanywa et al. (2020), demonstrated how a change in diet from grass to late summer crop and silage supplemented diets reduced the urinary-N load excreted by cows. Another successful management technique for reducing the urinary N load excreted on dairy pastures is achieved by standing cows off pastures once they have eaten their pasture allocation to ruminate and rest using

duration controlled grazing (Christensen et al. 2012). The use of feed-pads, stand-off pads and barns to feed supplements has increased. These facilities are used in winter to minimise soil damage, for animal welfare and to reduce N losses (de Klein 2001; de Klein, Smith, and Monaghan 2006). As mentioned previously (Chapter 2 and 4) dung and urine collected from the standoff facility is stored as slurry and when soil conditions are suitable, slurry is re-applied to land. Whereas this full or partial standoff of cows and subsequent slurry management successfully decreases urinary load and NO_3^--N leaching losses compared to cows permanently grazing pastures (Christensen et al. 2018) it is not clear whether volatilisation losses of NH_3-N from the urine and dung deposited and stored as slurry is greater or smaller than the urine patch deposited on pasture soil.

Various overseas studies (Castillo et al. 2000; ; Misselbrook et al. 2005d; Todd et al. 2006; Powell et al. 2008) and some NZ studies (Lazzarini, 2010; Totty et al. 2013; Kyamanywa et al. 2020) have been undertaken to address the dietary management strategies on cows performance, N portioning into milk, urinary urea, dung N. Few other overseas studies (Frank and Swensson, 2002; Misselbrook et al. 2005d; Elzing and Monteny, 1997) have considered the impact of diet on NH_3 volatilization losses from slurries, the NZ studies have not defined the influence of dietary management on NH_3 volatilization losses from urine patches or slurries. This Chapter investigates the effect of having dietary crude protein differences for late summer feeding of cows in New Zealand, on NH_3 volatilization losses from dung and urine slurries deposited on barn floors and from urine patches deposited on grass swards.

5.2 Materials and Methods

5.2.1 Urine and Dung Samples

Urine and dung samples were collected separately from 3 groups of dairy cows (each group containing 18 cows, total 54) on different crude protein diets (Kyamanywa et al. 2020). A high crude protein (HCP), medium crude protein (MCP) and low crude proteins (LCP) diet was fed to each group of cows respectively as presented in Table 4.1 (Chapter 4). For this study urine and dung samples were collected from cows in each mob and bulked to provide 3 separated single sources of dung and urine for this experiment (Table 5.1).

5.2.2 Chemical Analysis

As described in Chapter 4 Section 4.2.2.

5.2.3 Ammonia emission measurements

5.2.3.1 Ammonia emissions from slurry incubation

NH_3 emissions from the slurry mixture were measured in vitro in a laboratory set up at room temperature (18 ºC - 24 ºC) for 6 days as described in Chapter 4; section 4.2.3. Unlike, the slurry mixtures reported in Chapter 4, which were assembled with various urinary urea N concentrations whilst the dung N concentration was kept constant, in this experiment the urine and dung sampled from each dietary group was re-combined to create 3 different slurry samples simulating the slurry N content derived from cows on each of the 3 diets. Then the homogenised slurry mixture (23 g) was transferred from the urine container to the floor of the preserving jar (8 cm diameter), to give a slurry depth of 1 cm (Figure 5.1). An acid trap was immediately placed in the preserving jar with a polycarbonate sheet support. During the incubation of the slurry, acid traps were changed every 2, 4, 8, 16, 32, 64 and 128 h. The initial short interval acid trap change after 2 h was imposed to capture the NH_3 loss that simulated slurry remaining on a freestall barn laneway for only 2 h between lane scraper operations (Chapter 6). Sub samples of acid traps were taken for analysis of trapped NH_3^+-N by (colorimetric analysis) auto analyser (Novozamsky et al. 1983). Three replicate jars were used for each treatment and NH_3 emission flux was calculated as explained in section 4.3.3 of Chapter 4.

Figure 5. 1: Laboratory set up of measuring NH_3 emissions flux

5.2.3.2 Ammonia emissions from urine applied to intact soil cores

Another enclosure study was conducted to measure NH_3 volatilisation from the urine samples when applied to a pasture sward surface. In a separate set of Agee jars, urine

samples alone (33 ml) from each dietary group of cows were applied to intact pasture covered soil cores (65 mm diameter and 50 mm deep) contained in PVC drainage quality PVC tubing (Figure 5.2). Each application was replicated 3 times. Based on the analysis of the urine samples (Table 5.1), the rate of urine N application per surface area of the soil core was equivalent to 400 - 600 kg N ha^{-1}, a rate commonly reported for dairy cow urine patches (Selbie et al. 2015). The acid traps were changed every 12, 24, 48, 96 and 192 h for soil cores incubation.

Figure 5. 2: Laboratory set up of measuring NH_3 emissions flux from urine applied to soil cores

5.2.3.3 Soil core collection, preparation, urine application and mineral N extraction

The intact soil cores were collected in PVC drainage quality tubing from the top 50 mm of a clover ryegrass pasture on Pallic soil on Massey University No. 4 Dairy Farm (Feb, 2016). Each soil core was weighed and then air dried at room temperature for 3 days to create a soil water deficit that enabled urine to be applied without causing drainage. The cores were then placed in 1 L Agee jars and urine (33 ml) applied before incubating at 18 ºC - 24 ºC. Urine application rate was calculated based on the surface area of the soil cores (0.0033 m^2).

The soil samples were analysed at the end of incubation for mineral N. For mineral N extraction, the soil samples were sieved through 2mm sieve and then 5g of soil was

extracted with 50 ml of 2 M potassium chloride (KCl) solution followed by shaking for 1 hour. Then, the soil extracts were analysed for ammonium (NH_4^+-N) and nitrate (NO_3^--N) concentrations colorimetrically using Technion AutoAnalyser. Soil pH (air-dry soil sieved 2mm) was measured by using a Thermo Orion Star™ A214 bench top pH meter in the laboratory. The soil pH was measured at time zero just before sealing the preserving jars (1 : 2.5 soil : water ratio) and then after application of urine.

5.3 Statistical Analysis

The effect of manipulating dietary crude protein on urine and dung for total N, urea N, TAN and on NH_3 emission flux was analysed by ANOVA and comparison of means using Tukey's test at $p < 0.05$ by Minitab version 17 statistical software packages.

5.4 Results and Discussion

5.4.1 Effect of diet on excreta N composition

The urine and dung samples used in this study were collected during the study of Kyamanywa et al. (2020) who have already reported the significant reduction in urinary N concentrations when the diet of the cows was changed from grazed pasture (HCP) to supplementary grazed leafy rape (MCP) and leafy rape mixed with maize and grass silages (LCP) (Table 5.1). The chemical analyses of the accumulated bulk urine samples collected for this study showed that HCP and MCP had significantly higher urea N and TAN in urine compared to LCP while there was no significant difference in TN levels between the urine HCP and MCP (Table 5.1). The HCP and MCP dung samples had significantly higher TAN and TN compared to LCP dung samples. When combined into slurries HCP and MCP samples had significantly higher TAN and TN compared to LCP samples, but the TN and TAN of the MCP and HCP samples only differed by 2 to 3%.

Table 5. 1: Chemical composition of the urine and dung samples collected from each group of cows (n=3)

Parameters	LCP	MCP	HCP
Urine			
pH	8.07^a(0.02)	8.39^b(0.01)	8.4^b(0.01)
Urea-N (mg N L^{-1})	2449^a(27.2)	3936^b(25.4)	4032^c(32.1)

TAN (mg N L^{-1})	9.10(0.02)^{a}	15.5(0.04)^{b}	30.4(0.02)^{c}
Total N (mg N L^{-1})	4205^{a}(47.4)	5850^{b}(44.1)	5671^{b}(10.9)
Dung			
pH	7.01^{a}(0.03)	6.88^{b}(0.02)	6.77^{c}(0.04)
Dry Matter (%)	11.36	12.52	11.97
TAN (mg N L^{-1})	30.86^{a}(0.02)	62.02^{b}(0.04)	109^{c}(0.01)
Total N (mg N L^{-1})	2771^{a}(13.04)	2861^{a}(6.89)	3423^{b}(11.1)
Slurry			
pH	7.41^{a}(0.05)	7.59^{a}(0.01)	7.6^{a}(0.03)
Dry Matter (%)	7.81	8.13	8.25
TAN (mg N L^{-1})	1520^{a}(19.2)	1910^{b}(37.4)	2080^{c}(11.5)
Total N (mg N L^{-1})	3572^{a}	4548^{b}	469^{b}

Values between parentheses represent standard error of the mean (n=3)

Values with different superscript in a same row are significantly different ($P<0.05$)

All the values expressed on a fresh weight basis

Urine collected from the HCP, MCP and LCP cows contained 75%, 71% and 66% of total N as urea, respectively (Table 5.1). The HCP, MCP and LCP diets gave cows' daily N intakes of approximately 650, 500 and 400 g N cow^{-1} d^{-1} (Kyamanywa et al. 2020). The empirical dairy cow N partitioning model (Figure 5.3) created from other New Zealand feeding trials (Ordóñez et al. 2003; Bryant et al. 2010; Lazzarini, 2010; Totty et al. 2013) predicts that the urinary N load for the HCP would be 397 g N cow^{-1} day^{-1}, 3 fold greater than that of LCP diet (135 g N cow^{-1} day^{-1} and 1.6 fold greater than the MCP diet at 210 N g cow^{-1} day^{-1}. This predicted change in urinary-N load and the decrease in dung N load are consistent with the relative changes the measured urine N concentrations (Table 5.1) but the degree of model-predicted change in urinary N load is approximately twice the change seen urine concentrations. For example, the as CP concentration in diet is reduced from 25% (HCP) to 13.5% (LCP), the amount of the concentration of total urine N decreased from 5.67 to 4.2 (Table 5.1), a 1.35 fold reduction.

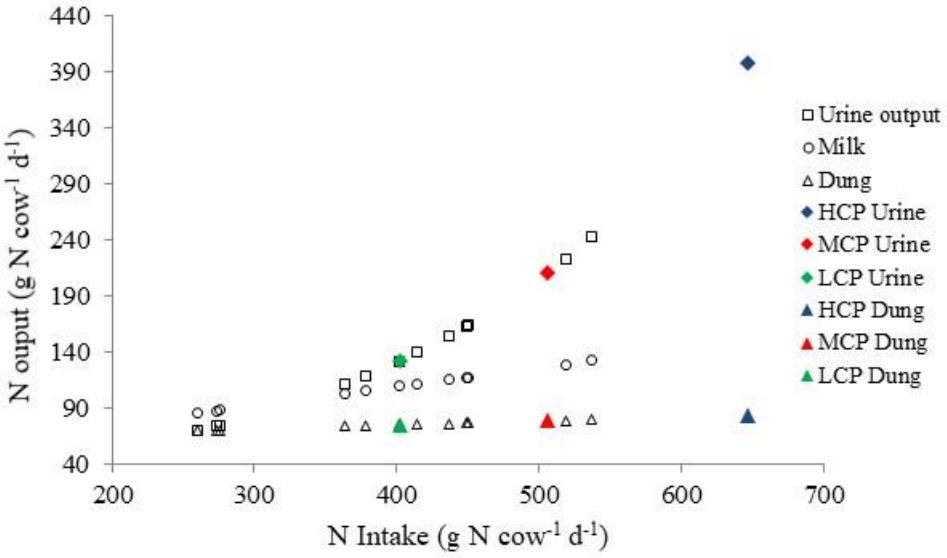


Figure 5. 3: N partitioning into milk and excreta from dairy cows on daily basis using empirical modelling based on NZ feeding trial data and three different crude protein diets (LCP, MCP and HCP) used by (Kyamanywa et al. 2020)

The range of values for the percentage of total urine N present as urea N (66 – 75%, Table 5.1) are in accordance with those reported by Petersen et al. (1998), who reported values of 64 to 94% of total urine N as urea N in urine of dairy cattle. The reduction of dietary crude protein intake also impacted dung total N which reduced significantly from 3423 mg N L^{-1} to 2771 mg N L^{-1} (Table 5.1). The pH of urine and dung was also affected by change in diet. Urine from the HCP diet had the highest initial pH, whereas the dung from the HCP diet had the lowest pH. Total N, Urea N and TAN concentration in individual urine and dung samples and in slurry mixtures also varied with crude protein content in the diet. On mixing the dung and urine to simulate the slurry that would arise from cows eating the LCP, MCP and HCP diets the ratio of urine TN: dung TN was 66%, 49% and 60% respectively.

5.4.2 Slurry Incubation and ammonia emissions

The trend in pH of the slurry mixtures over the incubation period are shown in Figure 5.4. The strong impact of urinary N concentration on slurry pH has already been discussed in Chapter 4. A similar trend in pH of slurry mixtures was also expected in this experimental work, a rise in pH was expected in first 24 hours after mixing the slurry and simulating manure deposition. High urease activity in the dung results in rapid urea hydrolysis and pH increase favouring NH_3 emissions (Hagenkamp-Korth, Haeussermann, and Hartung

2015). The rise in pH with time after slurry deposition also confirms the results reported in Chapter 4. High NH_3 emission flux (Figure 5.5) is associated with slurry pH remaining above 8.5, in the first 60 h of incubation in which 19 - 26% of the total applied TKN in slurry and 42-53 % (Figure 5.6) of the urine derived N (Figure 5.7) were emitted as NH_3. Cumulative NH_3 emissions expressed as % TN applied from slurry mixture in the preserving jars over 128 hours were not different between HCP and MCP whilst overall emissions from MCP were greater than HCP and LCP (Figure 5.7) because total N excreted in urine was higher than HCP and LCP. Higher absolute NH_3 emissions were associated with the higher CP containing diets (HCP and MCP) and lower crude protein levels in the LCP diet of the dairy cows resulted in lower NH_3 emission flux. The flux from LCP was significantly lower than the HCP and MCP but there wasn't any significant difference in NH_3 emission flux from HCP and MCP, presumably because the urinary urea and TKN loads in the HCP and MCP slurries varied little in concentration (Table 5.1). NH_3 emissions rose steadily over a period of time but there wasn't any substantial difference in pattern % N volatilised from all the dietary mixtures. According to Elzing and Monteny (1997) peak emission rate should be observed between 1 and 5 hours after excreta deposition on barn floors and should increase with the amount of urea hydrolysed, which increases as urea N concentrations in urine increase. In another dietary manipulation experiment on dairy cows (James et al. 1999) on observed peak in NH_3 emissions over a period of 12 to 24h and 96% of emitted NH_3 was trapped in first 24 h confirming that NH_3 emissions burst take place soon after mixing urine and dung.

The amount of NH_3-N loss expressed as percentage of total urea N and total N in the slurry mixtures applied over the 128h during in vitro measurements showed that NH_3 emissions reduced from 53 to 42% and 26 to 19%, with HCP and LCP diets. Empirical models (Castillo et al. 2000; Kebreab et al. 2001) also suggest that reducing dietary crude protein intake level should correspond to lower TKN and urea N excreted in urine which was confirmed in this study.

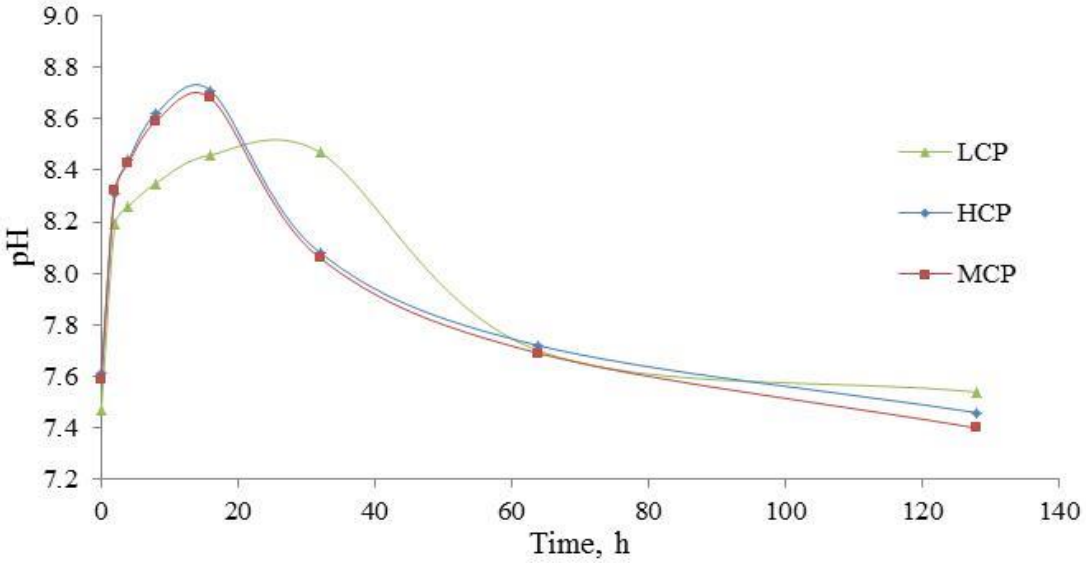


Figure 5. 4: The pH of slurry mixture incubated at (18 ºC - 24 ºC) in a closed system with different crude protein intake levels created by feeding dairy cows different crude protein diets over 128 h

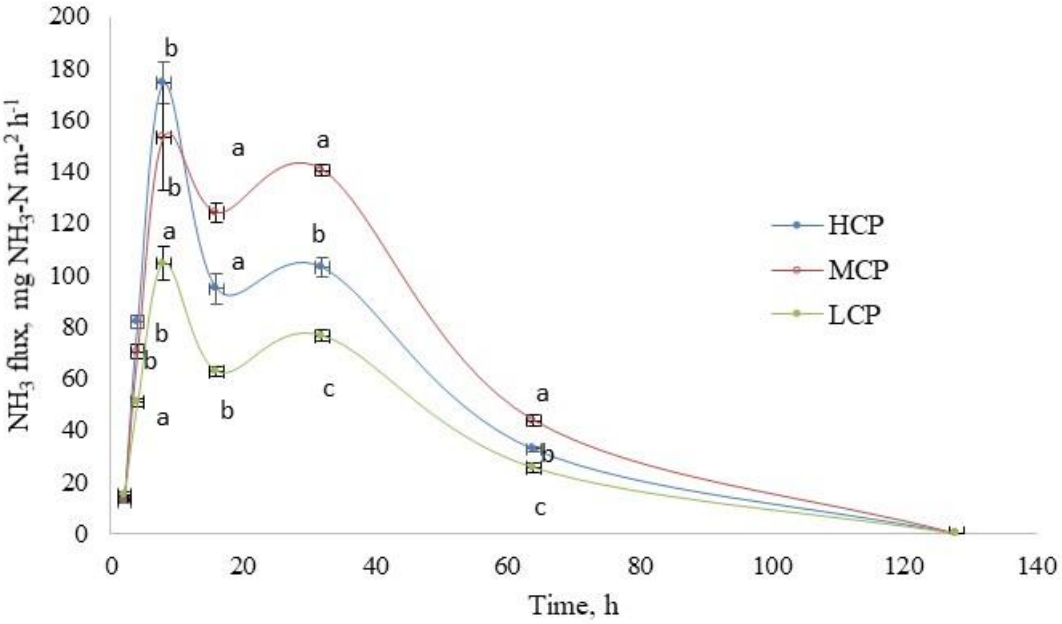


Figure 5. 5: Impact of manipulating dietary crude protein on average NH_3 emission flux (expressed as mg m^{-2} h^{-1}) from mixing urine and dung (10g dung : 13 ml urine) (w/v) to simulate manure deposition on barn floor. Vertical bars represent standard error of the mean (n=3)

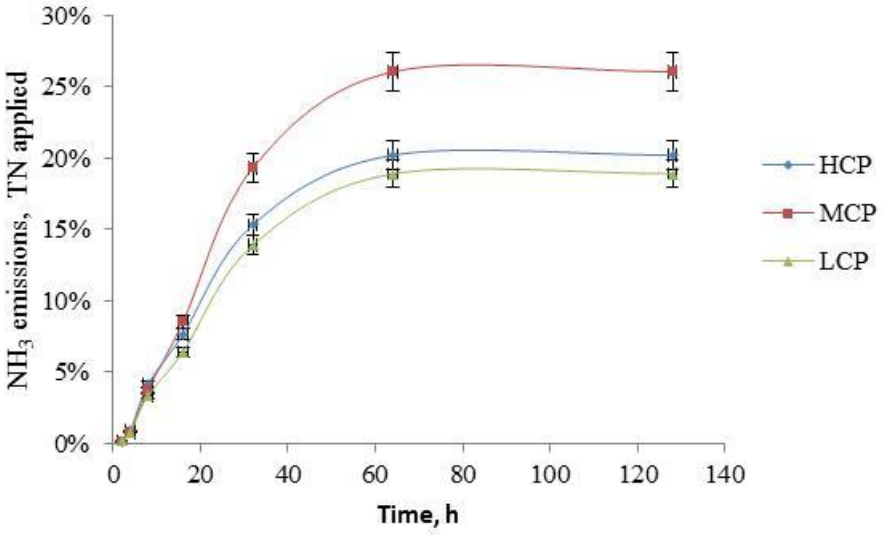


Figure 5. 6: Impact of manipulating dietary crude protein on average NH_3 emission flux (expressed as %TN applied) by simulating manure deposition (10 g dung : 13 ml urine) (w/v) on barn floor. Vertical bars represent standard error of the mean (n=3)

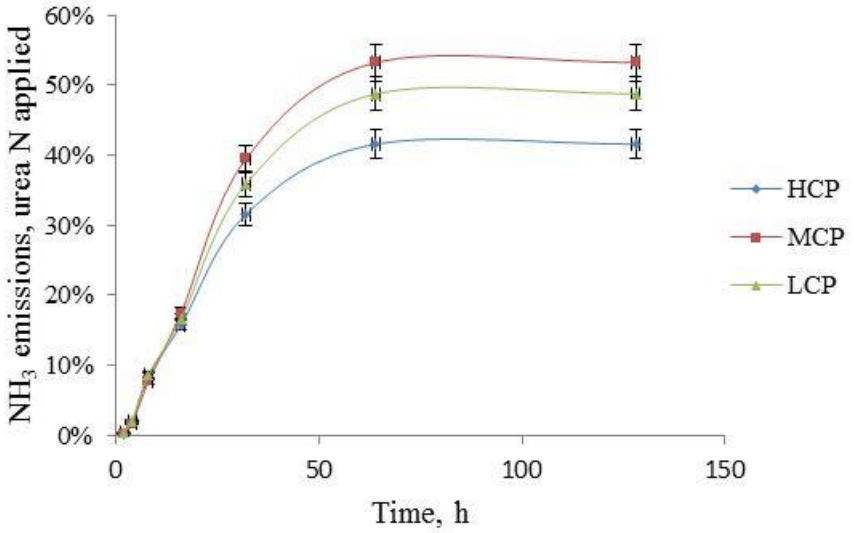


Figure 5. 7: Impact of manipulating dietary crude protein on average NH_3 emission flux (expressed as %urine N applied) by simulating manure deposition (10 g dung : 13 ml urine) (w/v) on barn floor. Vertical bars represent standard error of the mean (n=3)

5.4.3 Soil cores incubation and ammonia emissions

NH_3 emissions from urine applied to soil were less than 22 mg NH_3-N m^{-2} h^{-1} (Figure 5.8) as compared to emissions from the urine and dung slurries (maximum 175 mg NH_3-N m^{-2} h^{-1} (Figure 5.5). Less than 3% NH_3-N was lost during the 192 h of incubation from urine application with high urea N (HCP). Similarly with a high crude protein diet of

ryegrass/clover (HCP) the NH_3 emissions from soil were only 1% of total N higher than the MCP and LCP diets. This low % emission of the total N applied as urine is of similar scale to the NH_3 losses (< 4.5% of added urine N) from similar amounts of dairy cow urine applied to intact soil cores recorded by Singh et al. (2009). The amount was 2.54 times more than urine N applied to the soil cores than added to the slurry mixtures. Despite this NH_3 loss was low at <3% compared to 38.8 to 30.8% of urea N lost from the HCP and LCP incubated slurries during 128h of incubation (Figure 5.8). A 10 fold reductions in NH_3 emissions were observed when urine was not mixed with the dung but was applied to soil alone. The main reason for the low emissions from soil is that the soil buffers the pH of urine solution in soil as well as the soil providing cation exchange surfaces to hold the NH_4^+ ions generated in urea hydrolysis. For example the initial soil pH was 5.89 in the control, which rose to 6.12 after urine application and then dropped gradually over the experimental period. Losses of N from urine patches as NH_3 can vary largely depending on urinary N loading and soil moisture and temperature conditions. Losses of less than 5% of the total N deposited in the urine patch are not common and it is more common for measured NH_3 losses from dairy cow urine patches to range from 8 – 29% of total urine N applied (Sherlock et al. 2009).

Table 5. 2: Chemical analysis of the soil cores at the end of the experiment

	Cow diet providing source of urine applied to soil		
Parameters	LCP	MCP	HCP
NO_3^--N (g kg^{-1})	0.54[a]	0.56 [a]	0.58 [a]
NH_4^+-N (g kg^{-1})	0.01 [a]	0.15 [b]	0.13 [b]
Mineral N (g kg^{-1})	0.59 [a]	0.72 [b]	0.71 [b]

Values between parentheses represent standard error of the mean (n=3)

Values with different superscript in a same row are significantly different ($P<0.05$)

All the values expressed on a dry weight basis of soil

At the end of the incubation the inorganic N concentration (NH_4^+ and NO_3^--N) increased significantly in soil cores after the application of urine cores (Table 5.2). The total increase in mineral N in the soil accounted for 63 to 67% of the urine N applied. Immobilisation of N into soil organic nitrogen and denitrification will account for the remaining 30 – 34% of applied urine N unaccounted for.

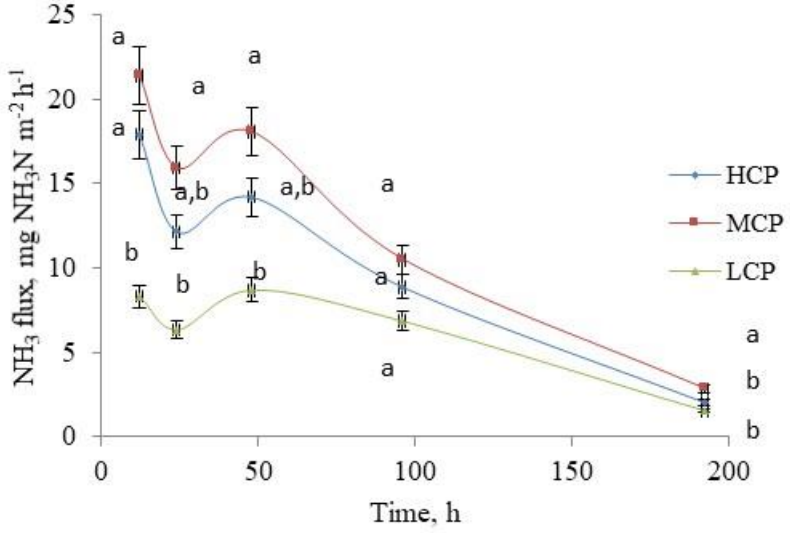


Figure 5. 8: Impact of manipulating dietary crude protein on average NH_3 emission flux from urine applied to soil cores (expressed as mg m^{-2} h^{-1}). Vertical bars represent standard error of the mean (n=3). Mean that do not share a same letter at each time period

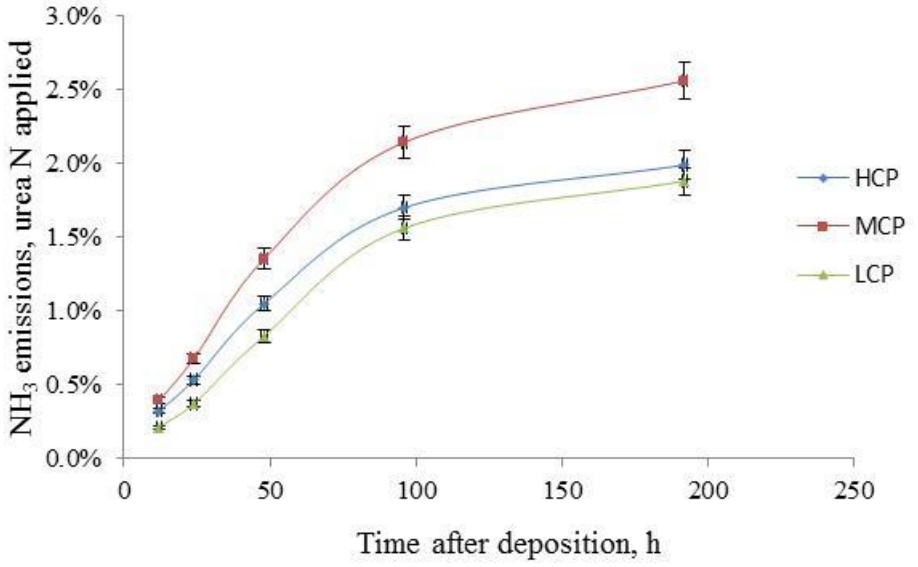


Figure 5. 9: Impact of manipulating dietary crude protein on % NH_3 emissions from urine application to soil cores (expressed as % urine N applied) by urine deposition (33ml urine) on soil cores. Vertical bars represent standard error of the mean (n=3)

5.4 General Discussion

A major concern with housing cows is the emission of NH_3 from slurry mixtures (Frank and Swensson 2002). This laboratory incubation study showed that manipulating CP content in diet could be used as a mitigation strategy for reducing NH_3 emissions from manure management chain. This study is conducted with freshly voided urine and dung,

in Chapter 4 dung N source was kept constant in order to determine the effect of urinary urea N on NH_3 loss. In the current experiment both dung and urine created by each dietary group of cows was recombined to simulate the slurry content that would exist on the barn floor housing cows on three different CP diets. Notably the NH_3 losses expressed as a % of urinary N added in this experiment (42 to 53%) were higher than those measured in Chapter 4 (17 % to 47 %) this is a direct consequence of the slurry surface area being greater and the slurry depth shallower in the experimental set up in Chapter 5. The relative effect of urinary N concentration on the absolute NH_3 volatilisation loss is similar for both experiments. In Chapter 4 and Chapter 5 a reduction in urea N concentration in the slurry from approximately 2200 - 2500 to 1400 - 1600 mg N L^{-1} slurry was associated with a 47% and a 37% reduction in NH_3 emissions, in Chapter 4 and Chapter 5's experiments, respectively.

Mainly, urinary urea concentration drives slurry pH and NH_3 volatilization confirming the results reported by (Kellems et al. 1979; Jarvis and Pain, 1990; Misselbrook and Powell, 2005; Sherlock et al. 2008; Sparks et al. 2011; Pereira et al. 2012) who performed dietary manipulation experiments under controlled laboratory conditions. Many overseas studies as reviewed by Ndegwa et al. (2008) and Sparks et al. (2011) showed that ammonia emissions from dairy cows can be controlled by manipulating N content in the diet. Different studies have been conducted on different scale and using different methodologies but all reported a positive relationship between dietary N intake on N partitioning into urine and dung and NH_3 emissions and urinary N plays a key role in driving NH_3 emissions. Elzing and Monteny (1997) reported linear relationship between N content in diet and NH_3 emissions, a reduced intake of N reduced the release of NH_3 from manure. Similar results were also reported by (Rotz 2004). In a seasonal dietary manipulation trials performed in a mechanically ventilated barn (Powell et al. 2008) also reported the positive relationship between N intake and NH_3 emissions. Pfeiffer et al. (1995) observed a strong correlation between CP intake and N excretion in urine and reported that CP over-supply, as well as amino acid imbalance, is one source for high amounts of urea excretion and results in low absorption coefficients. Rotz (2004) recommended that the most practical approach to increase N utilization efficiency by the herd is by manipulating pasture and crop N, use which in turn will reduce dietary CP and the N losses, particularly NH_3 volatilization from manure stores.

Recently in NZ, Totty et al. (2013) found that a diverse diet of chicory *(Cichorium intybus)*, plantain *(Plantago lanceolata)*, lotus *(Lotus pedunculatus)*, high-sugar ryegrass *(L. perenne)* and white clover *(T. repens)* influenced the CP content of the diet and led to a 17%–19% decrease in urinary-N content compared with ryegrass and white clover diets. NZ's pasture based diets are unique with very high crude protein content (average 13.5 to 25%) which is greater than any other dietary manipulation experiment reported in the literature (highest 19.8% reported by Smits et al. (1995). The results of Kyamanywa et al. (2020) clearly indicated that alternative late summer diets other than clover–ryegrass pasture can reduce the amount of urea N excreted in urine. The results in this Chapter show that if the cows are housed and offered alternative diets to clover ryegrass pastures then this can reduce NH_3 emission loss from fresh excreta slurries. One of the concerns is that the laboratory incubations indicate that contribution of urine N to the NH_3 loss is 10 fold greater if the urine combines with dung on a concrete surface compared to the NH_3 loss if the cow had deposited the urine on pasture. Separating urine and dung under barn conditions is difficult but studies conducted on separating pig urine and faeces in a mechanically ventilated barn have reported 99.3 % reduction in NH_3 emissions (Panetta, Powers, and Lorimor 2005). In another experiment performed on segregating cattle urine and dung (Vaddella et al. 2010) have reported 6 fold reduction in NH_3 emissions when urine away drained way from dung within the barn as compared to scraped manure. Realistically, it is impractical to minimise the contact between urine and dung particularly on a barn floor The low emissions from voiding urine only on soil cores provides an indication that cows at pasture, where dung and urine are separated, will generate much lower NH_3 emissions compared to cows in a barn.

5.5 Conclusions

The results from this study confirms that the common late summer autumn practice of introducing supplementary diets as alternatives to clover-ryegrass pasture reduces the dietary crude protein intake levels in dairy cows, significantly reducing urinary urea and total N in the dairy cattle urine and manure leading to reduced NH_3 emissions from combined urine dung slurries. These laboratory studies indicate that such dietary changes may reduce NH_3 emissions from combined urine dung slurries by 25%, which if this can be confined at farm scale, would contribute to reduced indirect N_2O emissions. In addition under the laboratory conditions of these experiment NH_3 emissions per unit of urinary N

were larger when urine is combined with dung, as in cattle yards, standoff pads and barns, compared to urine deposited alone on soil indicating that separate emission factors are required for urine deposited in barns and standoff compared to urine deposited at pasture. New Zealand needs more NH_3 emission measurements from urine deposited in barns and standoff pads to validate such an indication.

Chapter 6

Study of factors affecting ammonia gas emissions from a naturally ventilated dairy cow barn

6.1 Introduction

Although dairy cattle in New Zealand (NZ) are mainly grazed at pasture they are held in open standing yards for milking and feeding for up-to four hours per day for lactating cows (Shepherd et al. 2011). More recently three main types of housing, free stall barns, slatted floor Herd-Homes and deep litter barns have been introduced to hold cows for extended periods for feeding and rest when soils are wet and prone to treading damage (Christensen et al. 2019).

Dairy barn (feed pad or collecting yard) slurry (manure) is a mixture of urine and dung excreted by dairy cows. To keep free-stall barns clean slurry is scraped regularly from feed and bedding laneways to channels located underneath the barn floor that either store slurry, or transport the slurry to storage ponds. Dairy cows excrete >70 % of ingested N in the form of urea, which when combined with urease enzyme, prevalent in dung, produces ammonium and carbonate ions. Thus, fresh cattle slurry has a high pH (7+) and approximately 50% of total N exists as ammoniacal nitrogen ($NH_3 + NH_4^+$, TAN). Earlier studies, Chapters 4 and 5 demonstrated that ammonia emissions from fresh dairy cattle slurry were high in the few hours after deposition and are positively related to the concentration of urine-derived urea in the mixed slurry. It was found in these studies that, as the slurry ages urea concentrations and hydrolysis declines, slurry pH declines along with decline in NH_3 emissions.

The research summarized in this Chapter studies ammonia losses from slurry contaminated surfaces in a free stall barn used throughout the year, either for a short daily interval for feeding supplements (maize and grass silage) or full 24 h housing when soils are wet. The plan of the free-stall barn, which is a common design used in NZ, is presented in Figure 6.1 and 6.13. The sources of NH_3 emission surfaces are fresh slurry deposited in the four laneways and scraped to into the transport channel at four grate openings

(labelled Channel 1 to 4). The aged slurry as it passes down the transport channel (Channel Output) to the storage pond presents another emissions surface.

In Study 1 aged slurry samples (Experiment 1) were taken from different positions in the slurry pathway from channel grate to the storage pond (see Plate 1 (1a Laneways and grates, 1b Transport Channel, outside barn (Channel output) and Figure 6.13. In Experiment 2 (Ex-situ measurements), sources of fresh slurry were created (by mixing urine and dung) to represent the different depths of fresh slurry deposited in the free-stall barn's laneways and under the grates in the transport channel. The NH_3 emission rate from all slurry samples were measured in closed chambers. In study 2 (In situ measurements), a 3D sonic anemometer and NH_3 acid traps were used to measure airflow rates and NH_3 concentrations in the barns ventilation pathways. The barn's estimated NH_3 emissions calculated from the two contrasting studies are compared.

6.2 Factors that affect ammonia emissions from a naturally ventilated dairy cow barn

Dairy cow barns are designed and built in accordance with regional climate requirements, animal welfare, production objectives and to minimize environmental pollution (Angrecka and Herbut 2014; Ngwabie et al. 2009). Spatial and temporal variations in NH_3 concentrations can occur due to uneven distribution of urine and dung deposition, which are the main sources of NH_3 production and subject to change through animal movements and removal of slurry. In Chapters 4 and 5 it was shown that ageing of dung and urine slurry has an impact on and NH_3 emission rates. Therefore, within the free-stall barn slurry samples were collected from various scraper lanes, transport channel, and channel outflow to storage pond, which were then analyzed to determine spatial and temporal variation in chemical properties and NH_3 emissions. The details are given in following sections.

6.2.1 Experiment 1. Effect of temporal and spatial variation on chemical properties of and ammonia emissions from barn slurry

6.2.1.1 Free-stall barn plan

The study was conducted at the Free-stall Barn on Dairy farm 4, Massey University, Palmerston North. This research barn can house 200 cows with a space of 8 m^2 per cow. The dimensions of the barn are 70 m x 34.2 m (Length x Width) (Fig 6.1). The barn has an automatic scraping system scheduled every 2 hours and the excreta is mainly composed of urine and dung which is scraped every 2 hours to the transport channels located underneath the building where gravitational flow delivers manure to the outflow and finally ending up the in the uncovered storage pond.

Table 6. 1: Description of the cows and housing system

Housing system	Description
Housing type	Naturally ventilated
Cow number, breed	~200, Friesian/Jersey cross
Cow weight	`500 kg
Lactation length	~270 days
Milk production per cow	~ 453 kg MS cow^{-1}
Feeding	Pasture, maize and grass silages
Floor system	Concrete
Manure system	Slurry
Manure cleaning schedule	Every two hours, automatic scraper
Manure cleaning schedule	Gravitational flow from the transport channel pits to the storage pond (5 to 7 days)

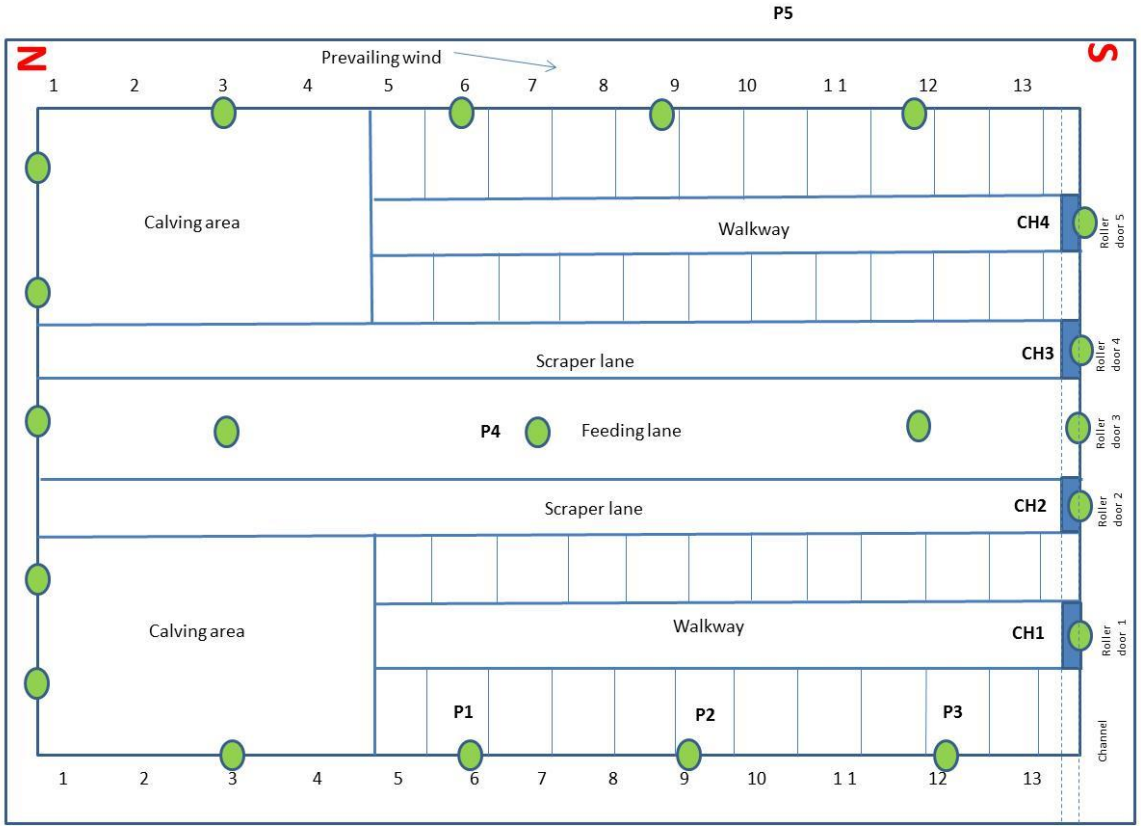


Figure 6. 1: Layout of the barn showing various locations for calving, the free-stalls and feeding lanes cows, transport channels (CH1 - CH4) and sampling positions for slurry samples (P1 - P5)

Channel 1 (CH1) to Channel 4 (CH4) are sampling positions at the end of lanes servicing the free-stalls, slurry scraped from these lanes is a mixture of dung and urine only. Channel 2 and 3 are sampling positions at the end of feeder lanes and from time to time split feed (maize and grass silage) is scraped into the channel which would change the chemical nature of the slurry being deposited in the transport channel.

6.2.1.2 Slurry sampling

Slurry samples were collected in duplicates from the scraper lane, transport channels and outflow vents on 5 separate occasions (Table 6.2 - 6.6). Samples were taken from the top 5 cm of the slurry (surface) and at 25 to 30 cm below the surface (sub-surface). Each slurry sample was analysed in duplicate for pH, nutrients and dry matter (DM) content. The detail of chemical extractions has been explained in Chapter 4 Section 4.2.2 of the thesis.

6.2.1.3 Statistical Analysis

The effect of different sampling dates and locations on dry matter (%DM content), pH, total ammoniacal nitrogen (TAN), total Kjeldahl nitrogen (TKN), total Kjeldahl phosphorus (TKP) and total potassium (TK) on chemical characteristics of slurry was determined by one-way ANOVA and comparison of means using Tukey's test at $p < 0.05$ by Minitab version 17 statistical software packages.

6.2.1.4 Results: Chemical analysis of slurry samples

The trend in chemical properties of manure for %DM content, TAN, TKN, TKP, TK and has been reported in Tables 6.2, 6.3, 6.4, 6.5, 6.6 and 6.7 respectively. The statistical analysis of the slurry samples showed that change in sampling location and date had a significant impact on nutrient analysis. The largest variance in the chemical properties of the slurry samples collected was caused by sampling date (Table 6.2 - 6.7), also the samples collected from the same channel but different depths varied significantly. The reason in variability of the samples is the deposition of fresh scraped slurry into the transport channels. The aged slurry stays in the transport channels for 5 to 7 days and continuous addition of slurry may cause alteration in the chemical composition of surface manure. The slurry deposition and mixing with the aged slurry depends on the gravitational flow and %DM content. Slurry with high liquid or urine content makes way to the pond rapidly, since the slurry in the channels is not agitated the rate of flow of the surface manure than the subsurface could also be possibly higher. There's no literature on spatial and temporal variation in chemical composition of the fresh and aged slurry samples collected from the various hot spots of cow barns.

Table 6. 2: Trend in %DM content of slurry samples collected from scraper lane, transport channels and outflow vents

%DM	Scraper lane mg L^{-1}	Channe1 surface mg L^{-1}	Channel1 subsurface mg L^{-1}	Channel2 surface mg L^{-1}	Channel2 subsurface mg L^{-1}	Channel3 surface mg L^{-1}	Channel3 subsurface mg L^{-1}	Channel4 surface mg L^{-1}	Channel4 subsurface mg L^{-1}	Outflow vent 1 mg L^{-1}	Outflow vent 2 mg L^{-1}
30/3/16	14.1^{a}	9.6^{g}	8.9^{h}	11.4^{e}	11.4^{e}	11.8^{d}	10.1^{f}	12^{c}	10.6^{e}	10.6^{e}	13.2^{b}
31/3/16	*	7.3^{h}	10.1^{e}	9.9^{f}	8.5^{g}	10.8^{b}	8.7^{f}	10.6^{c}	10.7^{b}	12.3^{a}	10.4^{d}
01/4/16	10.6^{b}	10.8^{a}	7.4^{e}	8.7^{g}	9.2^{c}	10.8^{a}	9.9^{c}	7.2^{f}	7.8^{d}	10.8^{a}	7.9^{d}
12/4/16	10.6^{g}	9.4^{h}	12.2^{c}	13.2^{b}	11.5^{f}	13.3^{b}	13.8^{a}	12^{d}	12^{d}	11.6^{e}	11.6^{e}
13/4/16	*	9.1^{i}	11.3^{e}	10^{f}	9.5^{h}	13.7^{b}	11.7^{d}	12.3^{c}	10.3^{e}	23.5^{a}	9.8^{g}
21/7/16	13.2^{a}	13.3^{a}	13.3^{a}	8.6^{f}	9.1^{e}	8.1^{h}	7.3^{h}	12.5^{b}	8.4^{g}	11.8^{c}	10.6^{d}

Values with different superscript in a same row are significantly different (P<0.05)
All the values expressed on a fresh weight basis

Table 6. 3: Trend in pH of slurry samples collected from scraper lane, transport channels and outflow vents

pH	Scraper lane mg L^{-1}	Channe1 surface mg L^{-1}	Channel1 subsurface mg L^{-1}	Channel2 surface mg L^{-1}	Channel2 subsurface mg L^{-1}	Channel3 surface mg L^{-1}	Channel3 subsurface mg L^{-1}	Channel4 surface mg L^{-1}	Channel4 subsurface mg L^{-1}	Outflow vent 1 mg L^{-1}	Outflow vent 2 mg L^{-1}
30/3/16	8.55^{a}	8.19^{b}	7.66^{e}	7.46^{h}	7.72^{d}	7.62^{f}	7.86^{c}	7.57^{g}	7.67^{e}	7.31^{i}	7.49^{h}
31/3/16	*	7.80^{b}	7.96^{a}	7.44^{e}	7.70^{c}	7.41^{f}	7.29^{g}	7.46^{e}	7.65^{d}	7.31^{g}	7.18^{h}
01/4/16	8.62^{a}	7.85^{f}	7.43^{i}	7.90^{d}	7.63^{h}	7.74^{g}	7.89^{e}	8.08^{b}	8.01^{c}	7.64^{h}	7.62^{h}
12/4/16	7.26^{e}	7.63^{b}	7.15^{g}	7.20^{f}	7.28^{e}	7.35^{d}	7.64^{b}	7.01^{i}	7.12^{h}	7.49^{c}	7.76^{a}
13/4/16	*	7.42^{g}	7.09^{j}	8.18^{a}	8.01^{c}	7.53^{e}	8.06^{b}	7.17^{i}	7.25^{h}	7.79^{d}	7.50^{f}
21/7/16	8.03^{c}	7.53^{b}	7.31^{f}	7.48^{e}	7.63^{d}	8.23^{ab}	8.09^{c}	8.75^{a}	8.40^{ab}	8.14^{b}	8.13^{b}

Values with different superscript in a same row are significantly different (P<0.05)
All the values expressed on a fresh weight basis

Table 6. 4: Trend in concentrations of TAN of slurry samples collected from scraper lane, transport channels and outflow vent

TAN	Scraper lane mg L^{-1}	Channe1 surface mg L^{-1}	Channel1 subsurface mg L^{-1}	Channel2 surface mg L^{-1}	Channel2 subsurface mg L^{-1}	Channel3 surface mg L^{-1}	Channel3 subsurface mg L^{-1}	Channel4 surface mg L^{-1}	Channel4 subsurface mg L^{-1}	Outflow vent 1 mg L^{-1}	Outflow vent 2 mg L^{-1}
30/3/16	519^{i}	1988^{b}	1661^{c}	1211^{f}	1673^{c}	1239^{f}	2213^{a}	749^{h}	1344^{e}	923^{g}	1532^{d}
31/3/16	*	1302^{c}	1863^{a}	1185^{f}	1715^{b}	690^{f}	982^{e}	1371^{c}	1615^{b}	1332^{c}	1174^{d}
01/4/16	614^{f}	1001^{e}	1323^{d}	1308^{d}	1340^{d}	1583^{bc}	1527^{c}	1902^{a}	1958^{a}	1316^{d}	1730^{b}
12/4/16	2599^{a}	1429^{cde}	1282^{def}	729^{g}	2175^{b}	800^{g}	1406^{cde}	929^{fg}	2091^{b}	1242^{ef}	1730^{bc}
13/4/16	*	1344b^{cd}	1323^{bcd}	2433^{a}	2352^{a}	716^{d}	2011^{ab}	932^{cd}	1677^{abc}	1373^{bcd}	1364^{bcd}
21/7/16	924^{f}	853^{f}	907^{f}	841^{f}	1071^{e}	1725^{d}	1850^{c}	2461^{a}	1911^{c}	1691^{d}	2063^{b}

Values with different superscript in a same row are significantly different (P<0.05)
All the values expressed on a fresh weight basis

Table 6. 5: Trend in concentrations of TKN of slurry samples collected from scraper lane, transport channels and outflow vent

TKN	Scraper lane mg L^{-1}	Channe1 surface mg L^{-1}	Channel1 subsurface mg L^{-1}	Channel2 surface mg L^{-1}	Channel2 subsurface mg L^{-1}	Channel3 surface mg L^{-1}	Channel3 subsurface mg L^{-1}	Channel4 surface mg L^{-1}	Channel4 subsurface mg L^{-1}	Outflow vent 1 mg L^{-1}	Outflow vent 2 mg L^{-1}
30/3/16	2673^{b}	3669^{ab}	3854^{a}	3623^{ab}	3362^{ab}	3387^{ab}	3169^{ab}	3687^{ab}	3608^{ab}	3272^{ab}	4371^{a}
31/3/16	*	2832^{ab}	2597^{ab}	2843^{ab}	3363^{ab}	2213^{ab}	2511^{ab}	2511^{ab}	3706^{ab}	4526^{a}	5864^{a}
01/4/16	4032^{abc}	2805^{c}	6024^{a}	3858^{abc}	2647^{ab}	2949^{ab}	2786^{ab}	4459^{abc}	3962^{abc}	3643^{abc}	5663^{ab}
12/4/16	6269^{a}	3300^{a}	3605^{a}	3821^{a}	4584^{a}	3215^{a}	3605^{a}	4675^{a}	2886^{a}	3905^{a}	7053^{a}
13/4/16	*	3261^{d}	3706^{cd}	4961^{a}	4906^{ab}	4474^{abc}	4459^{abc}	3704^{cd}	4201^{abcd}	4027^{abc}	4196^{abcd}
21/7/16	3828^{b}	4188^{ab}	3672^{bc}	2422^{d}	2787^{cd}	4110^{ab}	4131^{ab}	4080^{ab}	3741^{b}	4317^{ab}	4902^{a}

Values with different superscript in a same row are significantly different (P<0.05)
All the values expressed on a fresh weight basis

Table 6. 6: Trend in concentrations of TKP of slurry samples collected from scraper lane, transport channels and outflow vents

TKP	Scraper lane mg L^{-1}	Channe1 surface mg L^{-1}	Channel1 subsurface mg L^{-1}	Channel2 surface mg L^{-1}	Channel2 subsurface mg L^{-1}	Channel3 surface mg L^{-1}	Channel3 subsurface mg L^{-1}	Channel4 surface mg L^{-1}	Channel4 subsurface mg L^{-1}	Outflow vent 1 mg L^{-1}	Outflow vent 2 mg L^{-1}
30/3/16	356^{b}	609^{ab}	685^{ab}	737^{ab}	867^{a}	709^{ab}	543^{ab}	777^{a}	590^{ab}	861^{a}	929^{a}
31/3/16		446^{a}	375^{a}	466^{a}	515^{a}	450^{a}	458^{a}	568^{a}	712^{a}	808^{a}	401^{a}
01/4/16	919^{abc}	701^{abc}	824^{a}	516^{bcd}	447^{d}	812^{a}	629^{a}	469^{cd}	639^{abcd}	744^{ab}	531^{bcd}
12/4/16	793^{f}	606^{i}	841^{e}	1032^{a}	672h	870^{d}	752^{g}	962^{c}	544^{j}	793^{f}	981^{b}
13/4/16	*	662^{b}	835^{b}	657^{b}	698^{b}	1089^{a}	649^{b}	837^{b}	750^{b}	742^{b}	732^{b}
21/7/16	530^{c}	540^{abc}	675^{a}	266^{e}	304^{de}	568	587^{ab}	571^{abc}	433^{cd}	645^{ab}	562^{abc}

Values with different superscript in a same row are significantly different (P<0.05)
All the values expressed on a fresh weight basis

Table 6. 7: Trend in concentrations of TK of slurry samples collected from scraper lane, transport channels and outflow vents

TK	Scraper lane mg L^{-1}	Channe1 surface mg L^{-1}	Channel1 subsurface mg L^{-1}	Channel2 surface mg L^{-1}	Channel2 subsurface mg L^{-1}	Channel3 surface mg L^{-1}	Channel3 subsurface mg L^{-1}	Channel4 surface mg L^{-1}	Channel4 subsurface mg L^{-1}	Outflow vent 1 mg L^{-1}	Outflow vent 2 mg L^{-1}
30/3/16	1278^{k}	5139^{c}	6568^{a}	4660^{e}	4846^{d}	3600^{i}	3722^{h}	3932^{g}	6025^{b}	4478^{f}	3432^{j}
31/3/16	*	5179^{a}	4404^{e}	4067^{g}	3906^{h}	4830^{d}	4929^{b}	3860^{i}	4786^{c}	4225^{f}	2714^{j}
01/4/16	3429^{i}	5721^{c}	3458^{i}	3220^{j}	4944^{e}	4345^{f}	3818^{g}	3678^{h}	5029^{d}	6847^{a}	6729^{b}
12/4/16	3417^{i}	4902^{g}	3687^{h}	5066^{c}	7276^{b}	4659^{e}	4266^{f}	3680^{h}	8325^{a}	5301^{c}	4079^{g}
13/4/16	*	4156^{d}	4141^{d}	3194^{h}	5417^{c}	3665^{g}	8741^{a}	6062^{b}	3753^{f}	3807^{e}	2661^{i}
21/7/16	1270^{d}	729^{h}	7143^{a}	3169^{b}	2376^{c}	977^{e}	946^{f}	1262^{d}	949^{f}	906^{g}	1256^{e}

Values with different superscript in a same row are significantly different (P<0.05)
All the values expressed on a fresh weight basis

6.2.2 Experiment 2. Effect of slurry sampling location on Ammonia emission flux

6.2.2.1 Ammonia emissions measurements

Another laboratory incubation using 1 L Agee jars (Figure 6.2) was performed to study trends in NH_3 emission from samples collected to represent the slurry pathway from the laneway, through the transport channel to the storage pond (Figure 6.10). Fresh slurry samples were collected on (12/04/2016) from the scraper lane, surface (top 5 cm) of transport channel pits and the outflow vent. Sub samples of slurry were analyzed for pH, TAN (mg N L^{-1}), TKN (mg N L^{-1}), TKP (mg P L^{-1}) amd TK (mg K L^{-1}) and dry matter (%DM) content as described in Chapter 4 Section 4.2.2 of the thesis.

Figure 6. 2: A photograph of laboratory set up for measuring NH_3 emission flux from slurry sample collected from various locations of the barn

6.2.2.2 Statistical Analysis

As explained in section 6.2.1.3 and the relationship between influencing factors like initial pH, initial TAN with NH_3 emission flux and relationship between time averaged pH, initial TAN and cumulative NH_3 losses was determined by multiple linear regression using MS Excel 2013.

6.2.2.3 Results: Ammonia emissions from slurry samples taken from the transport channel pit.

The chemical analysis showed that change in sampling location had a significant effect on trend in TAN (mg N L^{-1}) and TK (mg K L^{-1}) and %DM content however, it didn't influence TKN (mg N L^{-1}) and TKP (mg P L^{-1}) in slurry samples. The pH of the slurry samples also changed significantly with change in sampling locations. The trend in pH of

slurry samples was further used to explore the relationship between pH and NH_3 emission flux. The fluctuation in pH was attributed to rate of NH_3 emission flux from the slurry samples. Chemical properties of the slurry samples collected on 12/04/2016 used for NH_3 emission measurements are summarized in Table 6.8

Table 6. 8: Chemical composition of the slurry samples collected on 12th April, 2016 from different locations in the free-stall barn (n=2) measured at time 0 during the NH_3 flux measurement.

Parameters	Scraper lane	Channel 1	Channel 2	Channel 3	Channel 4	Outflow vent
DM (%)	9.78^{e}	9.41^{f}	13.16^{b}	13.31^{a}	12.04^{c}	11.61^{d}
pH	7.26^{e}(0.015	7.98^{b}(0.009)	7.03^{f}(0.009)	7.96^{c}(0.001)	8.06^{a}(0.009)	7.57^{d}(0.012)
TAN (mg N L^{-1})	1242^{bc}(17.6)	1429^{ab}(13.5)	729^{c}(14.1)	800^{c}(15.2)	929^{c}(17.6)	1765^{a}(21)
TKN (mg N L^{-1})	6269^{a}(31.2)	3300^{a}(28.7)	3821^{a}(30.9)	3215^{a}(28.3)	4675^{a}(34.2)	6309^{a}(39.7
TKP (mg P L^{-1})	793^{a}(14.1)	606^{a}(12.3)	1032^{a}(16.1)	870^{a}(14.8)	962^{a}(15.5)	981^{a}(15.7)
TK (mg K L^{-1})	5301^{a}(36.4)	4902^{b}(35)	5066^{c}(35.6)	4659^{d}(34.1)	3094^{e}(27.8)	4079^{f}(31.9)

Values between parentheses represent standard error of the mean (n=2)

Values with different superscript in a same row are significantly different ($P<0.05$)

All the values expressed on a fresh weight basis

6.2.2.4 Trend in ammonia gas emission flux from slurry incubations

NH_3 emissions over first 24 hours from various slurry sampling locations showed that highest emission flux 45 mg NH_3-N m^{-2} h^{-1} was from Channel 4 followed by Channel 3, Channel 1, Outflow, Scraped and Channel 1 stored slurry (Figure 6.3). The high emission rate from channel 3 and 4 is a consequence of high pH. The higher the pH the higher the emission rate (Table 6.8). Ammonia emissions begin shortly after urine and dung are deposited and get mixed. Scraped slurry is a mixture of freshly deposited urine and dung less than 2 h old prior to delivery to the transport channel. Over a period of 6 days there was no significant difference in NH_3 emission flux rate from the slurry samples collected from the same location; however the flux rate changed significantly with change in location (Figure 6.3). The emissions from the aged slurry in this experiment also showed that 3 to 9% (Figure 6.3) of slurry TKN is lost as over 144 hours from the various locations within the barn. Channel 2 and 3 are sampling positions at the end of feeder lanes and

from time to time split feed (maize and grass silage) is scraped into the channel, which would change the chemical nature of the slurry being deposited in the transport channel. As expected, the location of channel 2 and 3 changed the %DM content of the deposited slurry in the transport channel, the mixing of feed in the slurry mixture resulted in high DM content which also impacted NH_3 emission flux (Table 6.8; Figure 6.3).

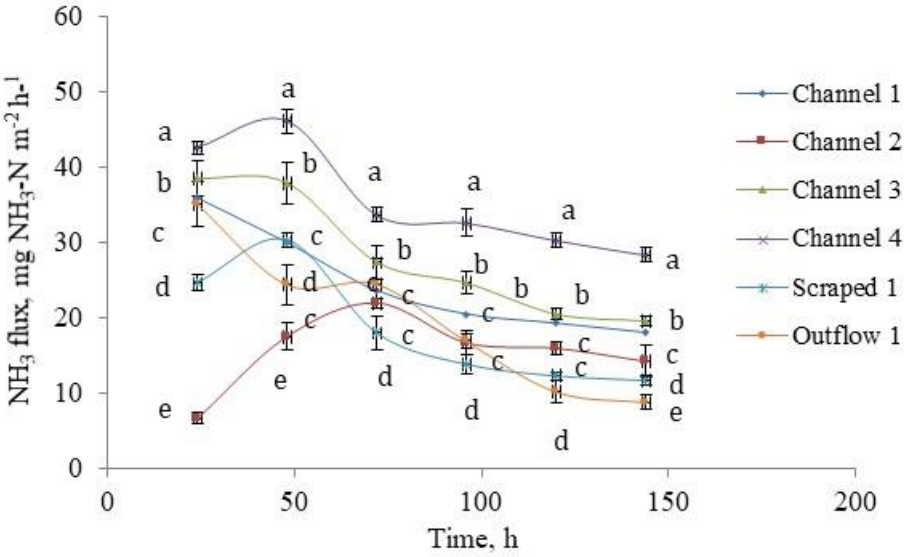


Figure 6. 3: Impact of different sources of slurry, scraped and under transport channel grates and the outflow on average NH_3 emission flux (expressed as mg m^{-2} h^{-1}) from 23 g of slurry sample in 1 L Agee jars (in situ measurements). Vertical bars represents standard error of mean.

The results from Chapters 4 and 5 show that during the first 2 h after urine and dung deposition and mixing there is a high NH_3 emission flux, up-to 175 mg NH_3-N m^{-2} h^{-1}. Then if the slurry stays in transport channel for 2 - 5 days with emission rates ranging from 9 - 30 mg NH_3-N m^{-2} h^{-1} a further 5 to 8% of total applied TKN will be lost as NH_3 (Figure 6.4).

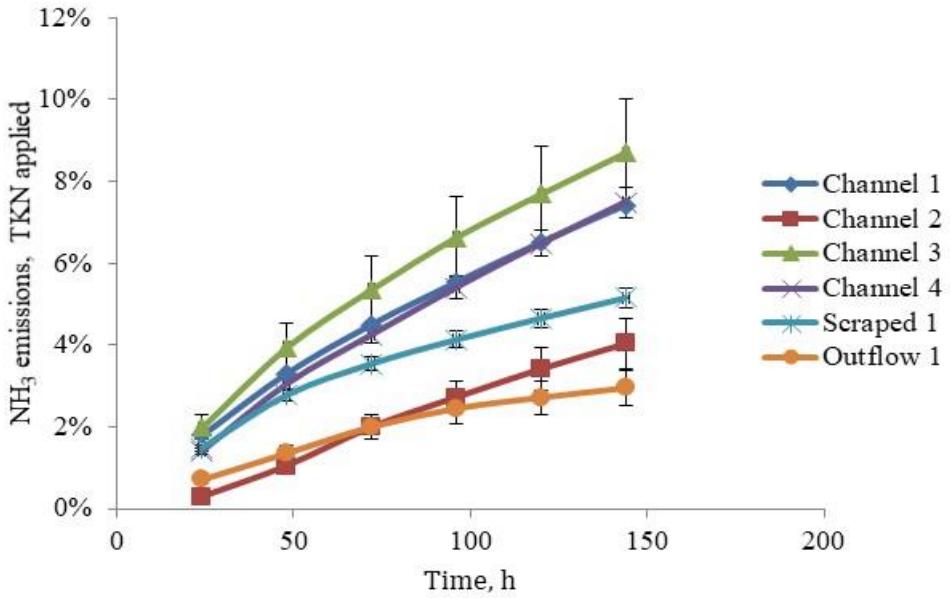


Figure 6. 4: Cumulative NH_3 losses from scraped slurry, transport channel grates and the outflow on average NH_3 emission flux (expressed as %TKN applied) from 23 g of slurry sample in 1 L Agee jars (in situ measurements). Vertical bars represent standard error of the mean.

6.2.2.5 Effect of pH of slurry on ammonia emission flux

The trend in pH of slurry samples measured every 24 h is shown in Figure 6.5. A rise in pH is expected in first 24 hours but for the slurry samples collected from various locations the time spent in that particular spot was unknown except for the freshly scraped slurry. The pH of the scraped manure was 7.26 at time zero indicating that the initialization of urea hydrolysis. As stated earlier, rise is NH_3 emission flux was related to rise in pH indicating that pH is the main factor driving NH_3 emissions.

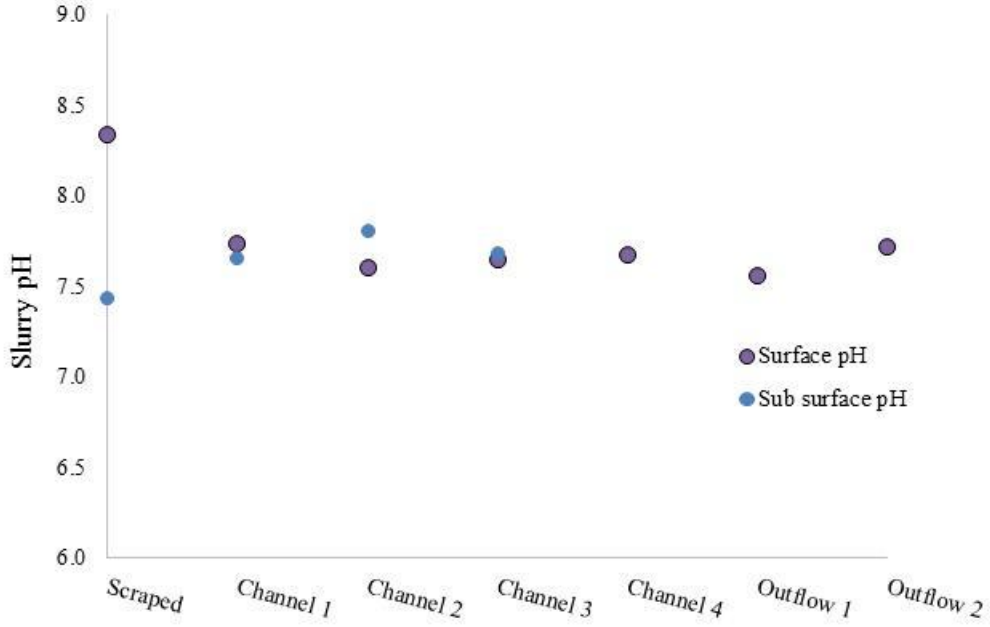


Figure 6. 5: Trend in pH of slurry collected from scraper lane, transport channels and outflow vent over a period of time (6 days)

This trend in pH was regressed against mean NH_3 emission flux to determine the relationship between both. A similar empirical modelling was conducted in Chapter 4 of this thesis using re-constituted slurry samples from mixtures of urine and dung. Here the regression is performed on data for the actual slurry samples collected from the transport channels and outflow vents.

6.2.2.6 Trend in initial TAN and pH of slurry samples collected from various locations

One of the objectives of the research is to find relationships that allow the NH_3 flux from slurry surfaces to be predicted. In Chapter 4 and 5 it was shown that the urea content of urine and the proportion of urine in the dung urine slurry have a major influence on the initial pH of the slurry. In the section above, the pH of slurry was found to influence NH_3 emissions over a period of time or as the slurry ages. In this section the initial pH and TAN of the slurry samples were investigated as predictors of NH_3 emission flux. The trend in initial TAN and pH changed significantly with change in sampling locations (Table 6.8). Multiple linear regression was used to determine the relationship between NH_3 emissions flux in first 24 hours against initial pH and initial TAN (Table 6.9) and average NH_3 flux over 144 h against averaged pH and initial TAN (Table 6.10)

Table 6. 9: Average NH_3 flux (mg m^{-2} h^{-1}) in first 24 h as a function of initial pH and initial TAN

Factors	Coefficients	SE	t stat	P value	R^2
Initial pH	27.79	3.2	8.6	0.0001	0.90
Initial TAN	0.0075	0.003	2.3	0.04	
Intercept	-190.59	24.48	-7.78	0.0002	

Table 6. 10: Average NH_3 flux (mg m^{-2} h^{-1}) over 144 h as a function of average pH and initial TAN

Factors	Coefficients	SE	t stat	P value	R^2
Initial pH	26.1	3.6	7.2	0.0025	0.87
Initial TAN	-0.003	0.001	-2.7	0.00008	
Intercept	-165.13	26.55	-6.21	0.0025	

From multiple linear regression models (Table 6.9 and 6.10), pH was found to be to the most significant and the most dominant factor explaining the variation in flux, and initial TAN remains a significant factor particularly when averaged NH_3 flux over a period of time is considered. This confirms the claim that the initial pH and initial TAN are very useful in predicting NH_3 emission flux in first 24 hours and as the slurry ages in the transport channel pits and outflow vents. Then, the relationship between measured/observed NH_3 emission flux and predicted NH_3 emission flux was determined using the coefficients of average pH and initial TAN (Table 6.10).

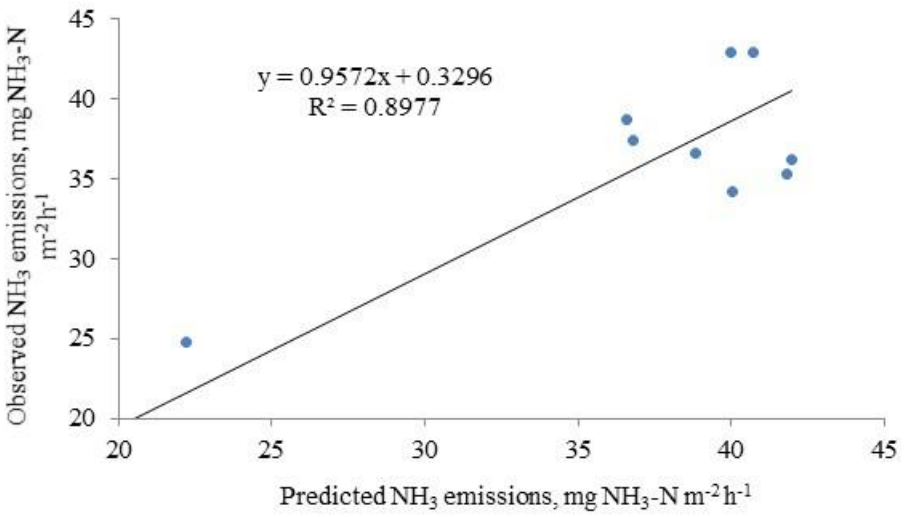


Figure 6. 6: Relationship between observed and predicted NH_3 emission flux obtained using the equation NH_3 flux (mg m^{-2} h^{-1}) = 26pH+0.003TAN-190.591

The above relationship which explains 89% of the variation in NH_3 flux supported the hypothesis that pH is the main factor responsible for NH_3 emissions from the slurry surface. According to (Kai et al. 2008) pH is among the main factor promoting NH_3 emissions, pH less than 6 - 7 will results in low emissions because of the high fraction of ammonium in TAN present in slurry. High emissions will occur at high pH above 7 due to the presence of high volatile ammonia fraction in TAN. NH_3 emissions from the partly covered indoor transport pits minimise the air exchange between the channel and the barn thereby lowering airflow above the slurry surface resulting in low NH_3 gas emissions (Rong, Nielsen, and Zhang 2009).

6.2.3 Experiment 3. Effect of fresh slurry depth on ammonia gas emissions

Every 2 hours layers of fresh slurry are delivered to the channel below the laneway grates below these fresh layers is older slurry. The scraped slurry remains in the transport channel for 5 to 7 days; the depth of the aged slurry in the channel was measured on several occasions which ranged from 50 cm to 80 cm. The highest slurry depth was observed for channel position 1 (80 cm) and lowest (50 cm) was recorded for channel 4. NH_3 is emitted from the surface of the slurry in the channel therefore it is important to understand how fresh slurry depth influences the rate of NH_3 emissions as well as the influence of aged channel slurry on NH_3 emissions rate.

6.2.3.1 Materials and Methods

6.2.3.2 Urine and dung collection

Fresh urine was collected (using 10 L buckets) directly from the back of 12 cows ('Housed cows') on the rotary milking platform during an afternoon milking session (08/11/2016) likewise fresh dung samples were collected directly from the back of 10 cows in separate 10L buckets. The urine and dung collected from different cows was algamated to form two separate bulk samples of urine and dung samples which were brought immediately to the laboratory. Then bulked urine and dung samples were mixed immediately to make slurry mixtures in the lab for incubations. The urine and dung were mixed in the proportions of 1 g dung : 1.3 ml urine (w/v) and added as different depth to the preserving jars. Sub samples of the urine and dung were retained for pH and elemental analysis as explained in Chapter 4 Section 4.2.2. Elemental analysis and pH was measured immediately after bringing the samples to lab (~20 minutes after collection).

6.2.3.3 Ammonia emission measurements

Ammonia emission collection commenced approximately 2 h after sample collection. A laboratory incubation experiment was set to study the impact of fresh slurry depth on NH_3 emissions. The set up details were replicated from Chapter 4 and 5 of this thesis; however the only difference was of positioning of passive acid traps in the enclosures. The acid traps were attached to the lids of the 1 L Agee jars for the ease of replacement. The acids

traps were replaced every 24 h for 6 days. Three fresh slurry depths (1, 5 and 10 cm) were selected; and repeated in triplicates (Figure 6.7). The laboratory set up and frequency of changing acid traps was the same as described in Chapter 5 Section 5.2.3.1.

Figure 6. 7: A photograph of laboratory set up for measuring NH_3 emission flux from various slurry depths

6.2.3.4 Results

The chemical analyses of the accumulated bulk urine and dung samples collected for Experiment 6.2.3 are reported in Table 6.10.

Table 6. 11: Chemical composition of the urine and dung samples collected from dairy cows during afternoon milking session and used in Experiment 1 (n=3)

Parameters	Urine	Dung
pH	8.36(0.015)	6.67(0.02) [a]
Dry Matter (%)	*	11.2 (0.03)
Urea (mg N L^{-1})	5853(3.6)	--
Total N (mg L^{-1})	5043(8.01)	3408 (86.9)[a]

Values expressed on fresh weight basis of fresh samples

a TAN= Total ammoniacal N

values in parenthesis represent standard error of the mean (n = 3)

6.2.3.5 Ammonia Emissions Flux

Profiles of ammonia gas emission flux and cumulative ammonia losses from different fresh slurry depths are reported in Figure 6.8 and 6.9. The highest flux rate 45 mg NH_3 m^{-2} h^{-1} was observed from 10 cm followed by 35 mg NH_3 m^{-2} h^{-1} from 5 cm and 32 mg NH_3 m^{-2} h^{-1} from 1 cm depth of slurry (Figure 6.8). The flux was highest over first 24 hours, declining uniformly over a period of time from all the depths. Although the volume

of manure stored in 10 cm depth was 3 times greater than that stored at 1 cm, it appears to have a little or no impact on magnitude of NH_3 emissions per unit surface area. As discussed in Chapter 4, the flux of NH_3 from slurry is a process limited by not only the pH of the slurry but the rate of NH_4 and $NH_{3(aq)}$ diffusion to the surface of the liquid and NH_3 diffusion from high concentrations at the slurry surface to lower concentrations in the atmosphere above. Similar results were reported from two other laboratory incubation experiments, the first experiment was performed on chicken manure stored at 5, 10, 20 and 40 cm (Li and Xin 2010) and the other one (Wang et al. 2014) was performed on biogas digester effluent stored at different depth. These authors also did not find a strong correlation between manure/slurry storage depth and rate of emissions.

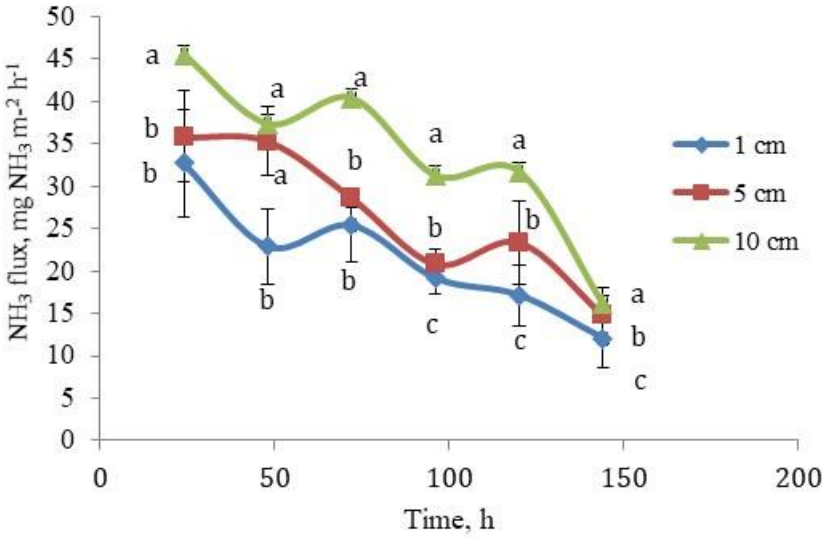


Figure 6. 8: Impact of different fresh slurry (10 g dung : 13 ml urine) (w/v) depths on average NH_3 emission flux (expressed as mg NH_3-N m^{-2} h^{-1}). Vertical bars represent standard error of the mean (n=3). Mean that do not share a similar letter at each time period are significant

The cumulative NH_3 emissions expressed as %TKN applied was highest for the 1 cm (14%) depth followed by 5 cm and 10 cm (1%) as shown in (Figure 6.9). These results and from (Chapter 4 ,5) indicate that urine urea concentration, slurry pH, the age of slurry, and the surface area (laneways) covered by fresh slurry rather than the volume of slurry will be the major drivers of NH_3 emissions in the barn.

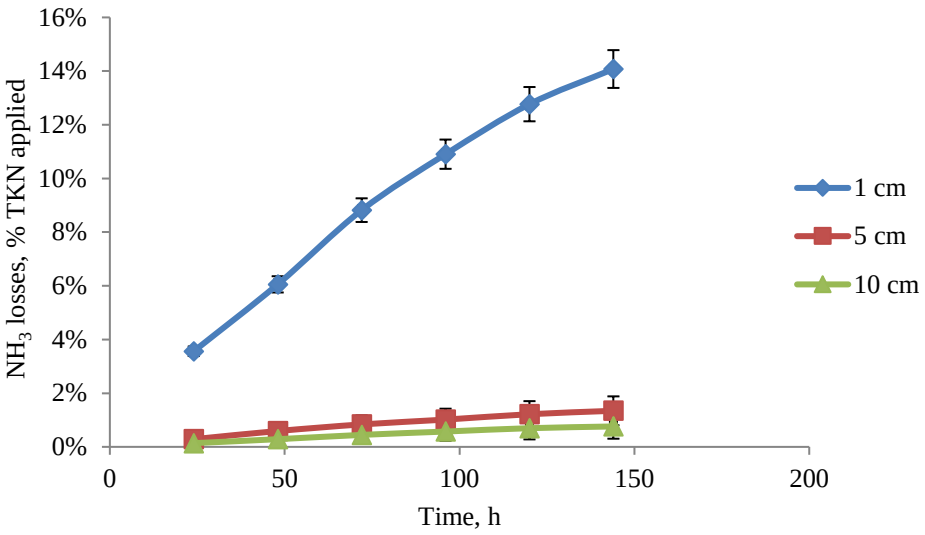


Figure 6. 9: Impact of different transport channel depths on cumulative NH_3 losses by simulating slurry deposition (10 g dung : 13 ml urine) (w/v) in a transport channel. Vertical bars represent standard error of the mean (n=3).

6.3 Experiment 4

6.3.1 In Situ ammonia emissions from the barn

According to (Ngwabie et al. 2009, 2014) the quality of gas concentration data can be improved by measuring short time variations within 24 hours and long term measurements to cover daily variations and seasonal variations can be addressed by intermittent measurements. In a naturally ventilated barn, the presence of many air inlets and outlets depending on the wind direction and wind flow makes the choice of sampling location hard. Emissions rates needs to be calculated from at-least one indoor and one outdoor locations from a barn (Aarnink et al. 1996; Blanes-Vidal et al. 2008). The choice of sampling location and monitoring ventilation rate didn't favour the long term emission measurements, therefore in this chapter a case study of active NH_3 gas measurements and monitoring ventilation rate is presented.

6.3.1.1 Housing system and position of airflow and active ammonia samplers

A plan of the naturally ventilated dairy barn (70 m x 34.2 m (Length x Width) with 7.14 m high ceilings and 37 main openings/ventilations) shows the position of airflow and active NH_3 samplers (Fig 6.1).

6.3.1.2 Production and feed information

The barn periodically housed Holstein dairy cows with feeding information shown in Tables 6.9 and 6.10. The average animal live weight was obtained from production sheets provided by management. During the period of study there was a fixed feeding schedule with feed delivered 1 or 2 times per day for the dairy cows. The daily diet composition is shown in Table 6.12.

Table 6. 12: Information on number of cows, housing hours and diet fed to the housed cows during the measurement periods

Dates	No. of cows	Housed Hours	Pasture (grazing)	Maize Silage (fed in barn)	Grass Silage (fed in barn)	Meal (fed at milking)	PKE	Intake g N cow^{-1} day^{-1}
30/03/2016	191	15	6	4	4	1	0	404
31/03/2016	191	15	6	4	4	1	0	404
0//04/2016	191	15	6	4	4	1	0	404
12/04/2016	189	0	11.5	2.5	0	1	0	520
13/04/2016	189	0	11.5	2.5	0	1	0	520
21/07/2016	73		10	2	1	2	1	516

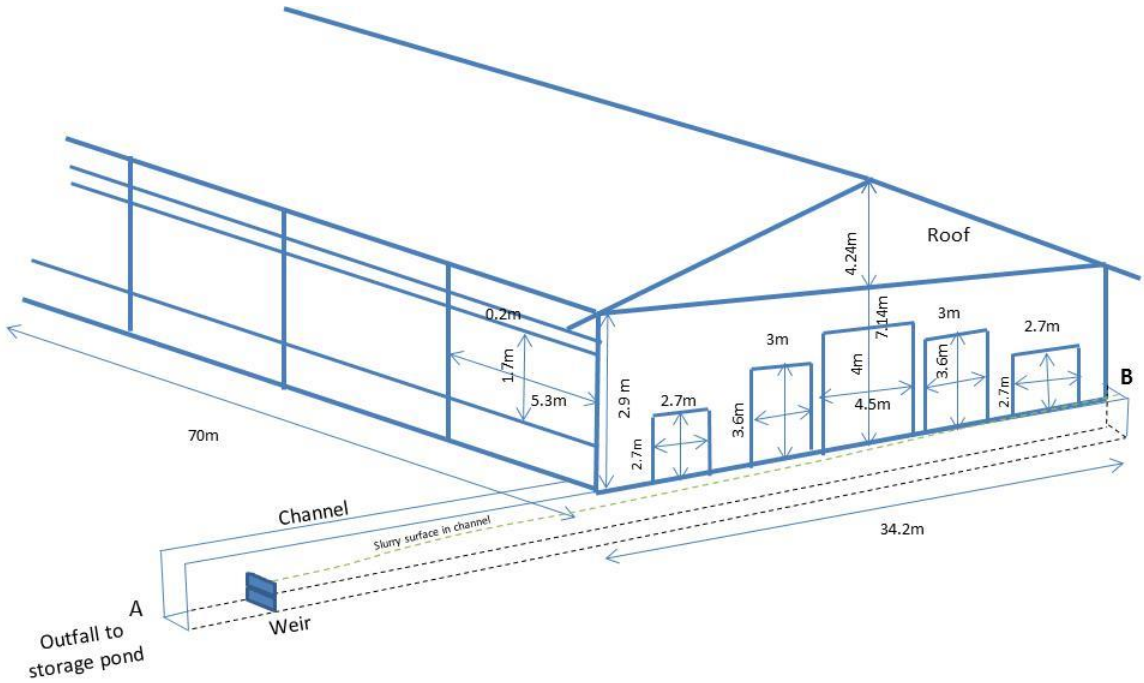


Figure 6. 10: Layout of the cross sections of the barn (South and West)

6.3.2 Materials and Methods

6.3.2.1 Measuring ammonia gas concentrations

Multiple-location air sampling for gas concentration measurements was carried out in the naturally ventilated dairy cow buildings. The NH_3 gas concentrations inside and outside the barn were measured by placing active acid scrubbers (6.11) at various positions (Figure 6.12) based on the wind direction as predicted by Met Services NZ (https://www.metservice.com/rural/manawatu). The details of the methodology have been described in Chapter 3; section 3.4.4 of this thesis. The indoor or outdoor concentrations of a gas at any time were the mean from all the indoor or outdoor sampling locations. A single outdoor sampling location (P5) and multiple indoor sampling locations (P1 - P3) were chosen inside the barn based on the wind direction prediction and one of the acid scrubbers was placed in the roof top vent (P4) along with the 3D sonic anemometer to estimate the volume of air flowing through the roof vent (Figure 6.11 and 6.12).

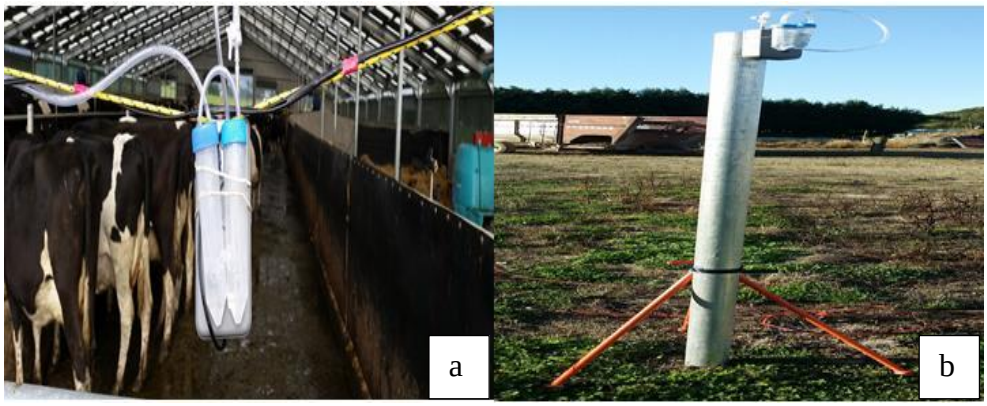


Figure 6. 11: Active acid scrubbers placed inside (a) and outside of the barn (b)

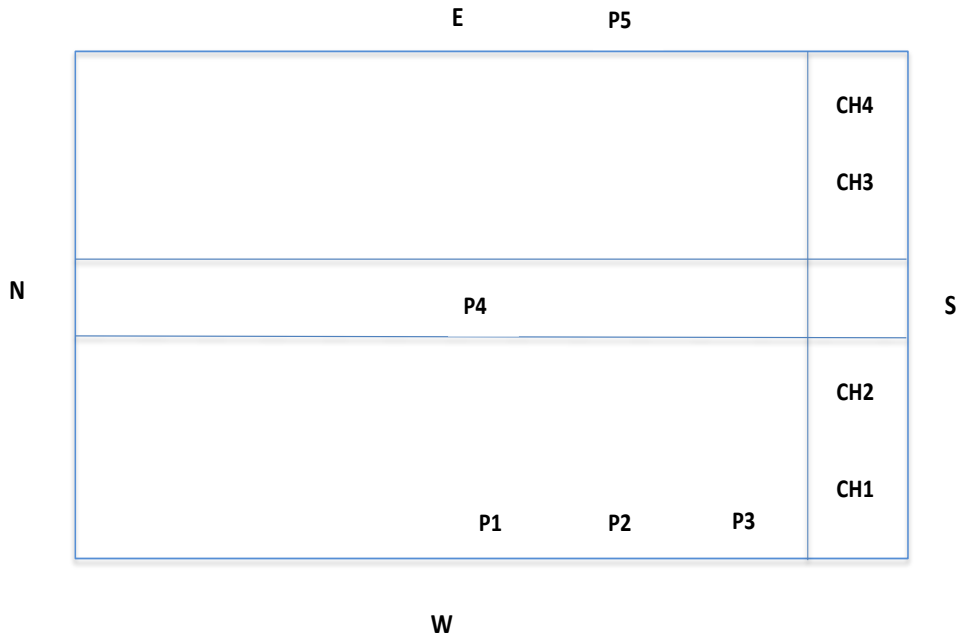


Figure 6. 12: Figure showing examples of the various positions of the active acid scrubbers placed inside and outside the barn

6.3.2.2 External and Internal Climatic Data Acquisition

In a NV dairy barn the most straightforward and direct method to monitor ventilation rate is by measuring airflow velocities at various openings of the barn by using multiple 3D sonic anemometers (Joo et al. 2014; Wang et al. 2016). It is difficult to determine the ventilation rate in naturally ventilated buildings due to the presence of many air openings, which can serve as both air inlets and outlets depending on the wind direction and thermal buoyancy. For ventilation rate measurements the position of air flow into the barn (air inlet) and position of air flow out of the barn (air outlets) varies with external wind direction and speed. The ventilation rate is therefore directly influenced by external and internal conditions in naturally ventilated buildings (Bruce, 1978; Snell et al. 2003).

Figure 6. 13: Orientation of the 3D sonic anemometer facing north placed at north side of the barn

For this study the internal wind velocities were monitored by moving the 3D sonic anemometer (Model 81000, R.M. Young Co.,Traverse City, MI) to various fixed openings within the barn, whilst simultaneous records of external wind direction and air velocities were recorded using a weather station (Model XC0369) mounted and positioned at north end of the slurry storage pond. The 3D sonic anemometer was always orientated north (Figure 6.13) when placed at different openings of the barn for internal data acquisition. Wind direction N to S and E to W is indicated by a positive velocity and S to N and W to E are indicated by negative wind velocities. As there was only one anemometer the measurement of wind velocities at doors and openings was discontinuous whereas the measurements of external wind direction and speed were continuous. The experimental objective was to create algorithms that would be able to predict the wind direction and ventilation rate at doors and opening from the continuously measured external data. Internal measurements were recorded for a period of 5 minutes before moving the anemometer to the next fixed position. This pattern continued for the whole measurement period. The data collected for the barn doors and openings was synchronized with the external wind direction and velocities data. The data for ventilation rate modelling was recorded in October and November, 2015 on 15 occasions when the

cows were not housed for the ease of moving anemometer throughout the barn. On the days when NH_3 gas emission measurements were made, anemometer was placed in the roof vent based on the assumption that roof vent continuously makes major contribution to the ventilation through the barn. Because the anemometer was in the roof vent we had to model the ventilation rate through the side openings of the barn using that model. Multiple regression analysis was used to establish relationships between external wind direction and velocity and the airflows into and out of the barn.

6.3.3 Results

6.3.3.1 Ammonia gas concentration in the air

NH_3 gas concentrations in the air (mg m^{-3}) measured inside and outside the barn on two occasions are presented in Table 6.13. The gas concentrations measured inside the barn were higher than outside due to the presence of cows and large volume of urine and ding deposition on the barn flour and transport channels. The highest concentrations were measured in the roof vent because of the large volume of ventilation taking place mainly through the vent.

Table 6. 13: Information on the active sampling of NH_3 gas in the barn

Sampling date	Position of the acid scrubber	Average flow rate of the pump (L min^{-1})	NH_3 concentration in the acid trap mg L^{-1}	NH_3 concentration in the air mg m^{-3}
30/3/2016	P1	1.3	60.6	0.36
30/3/2016	P2	1.4	41.1	0.21
30/3/2016	P3	1.1	19.9	0.13
30/3/2016	P4	1.6	118.1	0.39
30/3/2016	P5	1.0	1.42	0.01
31/3/2016	P1	1.2	84.1	0.64
31/3/2016	P2	1.4	107.5	0.66
31/3/2016	P3	1.0	9.21	0.06
31/3/2016	P4	1.5	136.4	0.66
31/3/2016	P5	1.1	3.7	0.03

6.3.3.2 Ventilation rate measurements, modelling and predictions

The polynomial algorithms developed from the external and internal wind direction and wind velocity measurements were used to predict a continuous set of wind direction and wind velocity data for each ventilation opening in the barn. The airflow rate through each opening was calculated based on the area of the opening coupled with measured wind velocities for a particular time period (Wang et al. 2016). For example Table 6.14 shows results of multiple linear regressions performed at North openings of the barn.

Table 6. 14: Table of multiple regression analysis of external wind vectors and flow through North openings of the shed through October and November, 2015 measurements

Factors	Coefficients	SE	t stat	P value
North wind velocity **(**$m\ s^{-1}$)	0.34	0.07	4.9	$1.2x10^{-5}$
East wind velocity **(**$m\ s^{-1}$**)**	-0.0005	0.002	-0.19	-0.006
Intercept	0.73	0.13	5.3	$3.6x10^{-6}$

The intercept and coefficients obtained from the regressions analysis were combined was used to estimate the wind run through N openings coupled with ammonia gas concentration data to predict kg NH_3-N losses. Based on the polynomial regression relationships obtained from the modelled data the airflow rate through each opening was calculated (Table 6.14)

Table 6. 15: Table of coefficients from multiple regression analysis of external wind vectors and flow through shed walls over the entire measurement period (October-November, 2015)

Coefficients	Ventilation walls			
	North	East	South	West
North wind velocity ($m\ s^{-1}$)	$3.4\ x10^{-1}$	$-2.5\ x10^{-1}$	$1.1\ x10^{-1}$	$2.1x10^{-1}$
East wind velocity ($m\ s^{-1}$)	$-5.4x10^{-4}$	$5.9x10^{-1}$	-0.19053	$5.8x10^{-1}$
P values intercept	$3.6x10^{-6}$	$1.2x10^{-15}$	$3.6\ x10^{-3}$	$9.2x10^{-15}$
P values North	$1.2x10^{-5}$	$6.5x10^{-4}$	$9.7\ x10^{-4}$	$1.4x10^{-1}$
P values East	$8.4x10^{-1}$	$4.0x10^{-10}$	$2.5x10^{-6}$	$1.3x10^{-8}$
Intercept	0.73844	-1.41462	0.179946	0

The ventilation rate through the roof vent was measured on two occasions for 16 hours when the cows were in the house. The measurements started at 4:00 pm in the evening until 9:00 am in the morning. During the gas measurements the total wind run (m) accounting the wind direction on through the roof vent on 30/31 March prevailing external wind direction was from the SSE (122 - 151 degrees) and total wind the roof vent is shown in (Figure 6.16). The wind run on the 30/31 was dominated by wind coming from 120 degrees (105 to 135 degrees) ESE while on 31-3 to 01-04 wind was unstable and with low values therefore the barn air flows became dominated by the intercept values which ideally should be 0 (Figure 6.14). The average ventilation rate through each opening and kg N loss is for both days are reported in table 6.15 and 6.16.

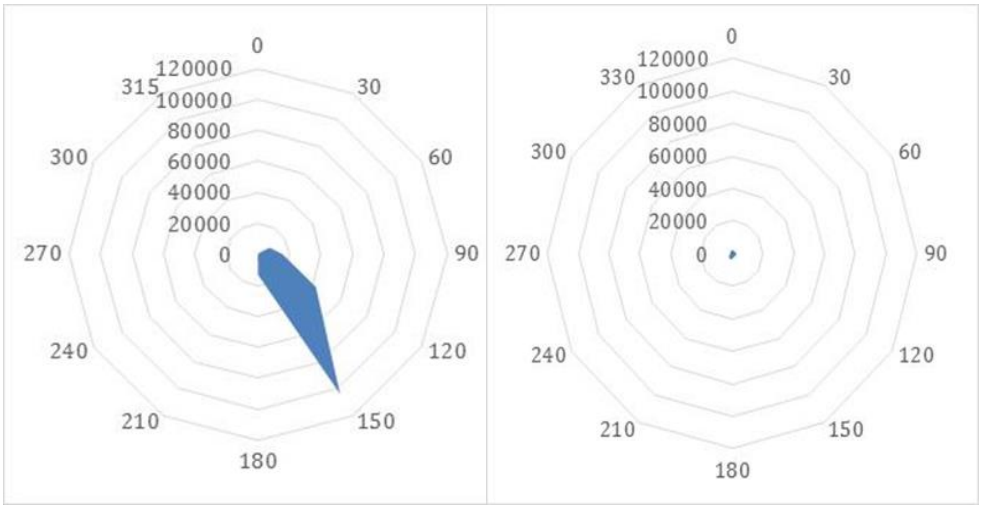


Figure 6. 14: Prevailing wind direction and the range of wind run (m) at the roof vent on 30/31 Mar and 31 Mar/1 Apr 2016

Air inlet into the barn occurred through the S and E ventilation openings and air outlet was from the N and W ventilation openings and the roof vent (Table 6.15). The outlet flow from the N opening was calculated as 10.8 x 10^6 m^3. At the W and central roof vents outflows of 5.5 x 10^6 and 4.5 x 10^6 m^3 were calculated and both had significant NH_3 concentrations (Table 6.16)

Table 6. 16: Information on measurement of ventilation rate through each barn opening for 16 h on 30-31/03/2016

Parameters	North	East	South	West	Roof Vent
Wind run (m)	$-7.4x10^2$	$1.8x10^4$	$-2.6x10^4$	$4.1x10^4$	$3.4x10^4$
Area (m^2)	242.82	133	54.18	133	133
Total air flow (m^3)	$-10.8x10^6$	$2.5x10^6$	$-10.4x10^6$	$5.5x10^6$	$4.5x10^6$
NH_3-N mg m^{-3}	0	0	0	0.23	0.39
Total NH_3-N kg	0	0	0	1.28	1.77
Total from barn NH_3-N kg					3.05

On day 2, air inlet into the barn occurred through the N and W ventilation openings and air outlet was from the E and S ventilation openings and the roof vent (Table 6.16). The inlet flow from the N opening was calculated as 5.9 x 10^6 m^3. At the W and central roof vents outflows of -10.8 x 10^5 and 2.3 x 10^6 m^3 were calculated , the wind run was low and unstauble resulting in overall low total wind flow through the roof vent.

Table 6. 17: Information on measurement of ventilation rate through each barn opening for 16 h on 31/03/2016 – 1/04/2016

Parameters	North	East	South	West	Roof Vent
Wind run (m)	$-7.4x10^2$	$1.8x10^4$	$-2.6x10^4$	$4.1x10^4$	$3.4x10^4$
Area (m^2)	242.82	133	54.18	133	133
Total air flow (m^3)	$-10.8x10^6$	$2.5x10^6$	$-10.4x10^6$	$5.5x10^6$	$4.5x10^6$
NH_3-N mgm^{-3}	0	0	0	0.23	0.39
Total NH_3-N kg	0	0	0	1.28	1.77
Total from barn NH_3-N kg					2.64

During the 16 hours measurement period on both occasions the barn air was replaced around 250 (30-31 March) and 180 times (31 March-1 April). The volume of air replaced explains the variation the kg NH_3-N losses (1.77 and 1.36 NH_3-N kg, respectively). In general under similar feeding and cow housing periods the larger the flow of air on a particular day the larger will be the losses.

6.4 General Discussion

Spatial variation in slurry chemistry and other factors affecting NH_3 emissions from a naturally ventilated dairy barn such as depth, external and internal weather conditions were studied in this chapter. The chemical analysis of the slurry samples collected on different days showed that sampling time, position and depth has an impact on chemical composition of the slurry particularly on pH and %DM content of the slurry. Temporal variation in gas concentration is caused by animal activity and scraping schedule. Slurry pH and not the TAN was found to be the main factor influencing NH_3 emissions as the slurry ages in the transport channel. A change in pH from 7.03 to 7.26 doubles the gaseous emissions. There was little or no impact of slurry depth on the magnitude of NH_3 emissions, the partial covering (iron mesh) above the slurry surface in transport channel pits restrict the airflow minimizing the air exchange between the shed and the channel which results in low gaseous emissions (Rong et al. 2014). Ventilation rates measured at 8 positions showed that any change in outdoor wind speed (m s^{-1}), wind direction (degrees) and temperature (ºC) would impact internal wind speed and direction. Ventilation rate over the emission surface is strongly influenced by the volume of air flow. High ventilation rate steepens the NH_3 concentration gradient at the slurry surface allowing more NH_3 to diffuse from liquid to gas phase, $[NH_3]_{gas}$ is the gaseous NH_3 concentration in equilibrium with NH_3 in solution (g NH_3-N m^{-3} air) whilst $[NH_3]_{ambient}$ is the concentration of NH_3 (g NH_3-N m^{-3} air) above air (normally very small). NH_3 volatilization from slurry surface should obey Henry's law and simple pH equilibria rules. The concentration of dissolved NH_3 in slurry and above the slurry surface can be related using Henry's law which indicates the partition between ionized and unionized form of NH_3 in slurry surface and air given by following equation

$$[NH_3]_{solution} \overset{K_h}{\leftrightarrow} [NH_3]_{gas} \qquad \text{Eq.6.1}$$

Where K_h is Henry's law constant (g NH_3-N m^{-3} air)/(g NH_3-N m^{-3} slurry).

Ventilation reduces the $[NH_3]_{gas}$ concentration at the slurry surface causing the reaction to move to the right.

The flux measurements performed using static enclosures on fresh slurry samples (Chapter 5) showed that freshly scraped slurry can emit ~100 mg NH_3-N m^{-2} h^{-1}, whereas emissions from slurry taken from the Channel emitted ~40 mg NH_3-N m^{-2} h^{-1}. Over the 16 h experimental emission of NH_3-N from the full lane surfaces and the channel would

be the sum of the products of emission rate and emission surface area. The emission estimates are presented in Table 6.17 and contribute a sum of 0.894 Kg NH_3-N (for 16 hours). These estimates are approximately 29% to 34% lower than those estimated from measuring NH_3 concentrations at the barn openings and the ventilation rate for 16h (sum of wall opening and vent losses 2.64 and 3.05 for the two 16 h periods, respectively. The airflow rate over the slurry scraper lane surfaces is obviously going to accelerate the emission rate. Whereas in the incubation jars the vertical flux of NH_3 was driven only by the diffusion gradient between the slurry surface and the acid traps. This gradient would only need to double the emission rate. In Chapter 3 (Figure 3.11) the rate of NH_3 emission collected from slurry in a passive acid trap in a preserving jar was compared to that collected by a dynamic acid trap. It was found that the passive trasp collected only 34 - 41% of the NH_3 released to the dynamic trap in the first 16 h. If this correction is applied to the NH_3 emission measured for lane slurries and channel slurries in preserving jars, then the estimates of the total barn NH_3 losses (derived from the passive incubation data) become 2.1 - 2.6 kg NH_3-N loss in for 16 hours, which is much closer to the loss (calculated from measuring NH_3 concentrations at the barn openings and the ventilation rate for 16h. When these rates of NH_3 emission, measured over 16h from 200 cows of approximately 500 kg liveweight cow^{-1}, are converted into NH_3-N g cow^{-1} d^{-1} the values 20 - 23 NH_3-N g cow^{-1} d^{-1} compare favourably with those (20 - 35 NH_3-N g cow^{-1} d^{-1}) for naturally ventilated barns in Sweden (Sanchis et al. 2018).

Table 6. 18: Information on NH_3 emission rates per m^2 from different locations of the barn

Location	Surface area m^2	Emission rate (mg NH_3-N m^{-2} h^{-1})	Emissions in 16 h (g NH_3-N)
Feed lane	283	100	0.453
Scraped lane	255.9	100	0.410
Transport channels	48.85	40	0.031
Total			0.894

In a naturally ventilated barn NH_3 capture and removal from the air stream is not an NH_3 reduction mitigation option. However cow diet manipulation may be an option. Based on the results of Chapter 4 and 5 manipulating crude protein content of diet can significantly

impact NH_3 gas emissions, which is the most practical and efficient way of lowering N excretion in excreta which lowers N gaseous emissions from the different stages of manure management. Manure is significant source of NH_3 gas emissions therefore strategically handling and managing manure is important to control gaseous losses from dairy cow barns. Removing manure from the barn is another way of lowering N emissions.

6.5 Summary and conclusions

Measurements of gas concentrations in naturally ventilated buildings were assessed. Factors that affect gas emissions, such as building parameters, management routines, climatic factors and parameters related to the animals were analysed. The following conclusions can be drawn from this research:

- Multi-location sampling of gas concentrations is necessary especially in naturally ventilated buildings for extended periods to cover all management and weather conditions that influence NH_3 sources and ventilation rates.
- Initial urea concentration of the slurry and pH are the main factors driving NH_3 emissions from the source but barn ventilation rates will accelerate or decelerate these losses significantly.
- Slurry collection and measurement of NH_3 loss using chambers is an option but this technique may underestimate NH_3 loss unless the chamber ventilation rate is varied to reflect barn ventilation rate changes.
- When trying to estimate NH_3 loss from barns slurry surface area is the most important variable rather than slurry depth.

Chapter 7

Ammonia gas emissions from a storage pond receiving effluent from a free-stall barn

7.1 Introduction

Slurry from the Massey University Dairy Farm no.4 freestall barn spends between 5 and 7 days in the channel (Chapter 6) at the ends of the scraper lanes before flowing by gravity into clay based effluent pond capable of storing 5707 m^3 .The effluent pond is emptied by tractor drawn slurry tanker when soil moisture conditions allow. On the mole and pipe drained Pallic soil at the farm a soil water deficit of 7 mm is required to provide soil strength for application by tanker and to allow 3 - 5mm of effluent to be applied without generating drainage. Over winter in the Manawatu 80 days may pass before a suitable soil water deficit is achieved. Effluent must be stored for this period**.** Ponds are the preferred method of effluent storage in New Zealand because of their low cost and easy maintenance. Slurry/effluent storage ponds are mostly used in NZ to store washed off excreta deposited around milking parlor and collecting yards. Ponds for storage of free-stall barn slurry are becoming more common as freestall barns are built to winter cows (van der Weerden et al. 2014).

One of the major drawbacks of using effluent pond is the odor and GHG emissions from the pond. Storage ponds are major contributors of GHG and NH_3 emissions even when managed actively to minimize the emissions (Amon et al. 2009; McGahan et al. 2016). Ponds are classified as aerobic, anaerobic and facultative depending on the biodegradation conditions. Most single storage ponds in NZ are anaerobic systems. In anaerobic ponds, excreta N is hydrolysed to ammonia, which exists in equilibrium as an ammonium ion or as dissolved ammonia gas. A rapid increase in pH shifts the equilibrium, placing more free ammonia in solution. Many factors for instance slurry handling, surface area of slurry storage pond, loading rate, environmental factors (e.g. evaporation, slurry age, slurry composition affect the NH_3 generation and emission process (Rotz et al. 2014).

There's limited NZ data on NH_3 emissions from storage ponds associated with freestall barns, partly because the difficulty and cost of measuring NH_3 losses is a major limitation. GHG and NH_3 emissions from dairy cow manure collected from housed cows in NZ have been measured in pilot scale experiments only (van der Weerden et al. 2014). This study is the first time that actual field measurements of NH_3 emissions from barn effluent storage ponds have been attempted. It's not known how the sampling method and various environmental factors like temperature, daily evapotranspiration rate are going to affect NH_3 emissions, therefore the main aim of these experiments was i) to develop a lost cost technique for long term field measurements and ii) to study the factors both environmental and slurry characteristics affecting NH_3 volatilization.

7.2 Materials and Methods

7.2.1 Slurry storage pond

7.2.1.1 Location of the Storage pond

The aerial photograph shows the location the effluent storage pond adjacent to the freestall barn. The slurry storage pond (semi triangle shaped) is located adjacent to the cow barn with maximum storage capacity of 5707 m^3 (Figure 7.1). The average fill pond depth is 2.3 m with a maximum full depth 4m to maintain bank integrity. Surrounding bunds minimize surface water intrusion. The full pond surface area is 0.112 ha. Gravity flow of slurry via the transport channels of the barn delivers the slurry to the pond. The composition of the channel slurry is explained in Chapter 6 of the thesis; since the pond is uncovered the addition of rainwater may alter the chemical properties of the slurry. The pond receives the largest volume of effluent from the barn mostly during winter when cows are housed to prevent treading damage of wet soils. Smaller volumes enter the pond during summer and autumn months when the barn is used 2 - 4 h per day for feeding of silages.

Ammonia emissions from the surface of the storage pond were measured over a short term (23rd to 28th August, 2016) and long term duration (2/06/2017 to 16/08/2017). The purpose of short term duration was to develop a reference method (passive versus active

NH_3 sampling) for measuring NH_3 emissions over longer periods with ease of deployment and analysis.

Figure 7. 1: An aerial view of the trial site showing location of the barn, storage pond and the paddocks (Google Earth, Nov, 2015)

7.2.2 Ammonia gas concentration Measurements

7.2.2.1 Active ammonia gas sampling

Ammonia gas emissions from storage pond were measured by active acid scrubbers for one week in August 2016. Details of this technique have been described in Chapter 3; section 3.5.2.1 of the thesis.

7.2.2.2 Passive ammonia sampling

Diffusion sampling tubes (DST) as described in Chapter 3 section 3.5.2.1 were used for passive NH_3 sampling. Simultaneous measurements of active and passive sampling were carried out for 24, 48, 72 and 96 hours.

7.2.2.3 The Integrated Horizontal Flux (IHF) Technique

Ammonia gas emission flux from the slurry storage pond was measured using micrometeorological mass balance and integrated horizontal flux methodology (Denmead et al. 1998; Ryden and Mcneill 1984) coupled with a weather station (model XC0369) mounted at north end of the pond to measure wind direction (degrees), wind speed (m s^{-}

^{1}) and air temperature (ºC). NH_3 gas profiles were recorded by using active acid scrubbers and diffusion sampling tubes (DSTs) mounted parallel to each other at heights (*h*) (0.25 m, 0.5 m, 1 m, 1.5 m, 2.25 m and 3.5 m) on the sampling mast mounted at all four banks of the storage pond. The active acid scrubbers were connected to an AC inverter which in turn was connected to 12 V car battery (EXIDE technologies) to actively pull the atmospheric air through the acid solution to capture NH_3. The placement of samplers at various heights allowed continuous measurement of NH_3 gas concentrations (C, mg N m^{-3}) in each horizontal flux layer. The horizontal NH_3 flux for each layer is calculated based on the product of NH_3 gas concentration in the acid trap placed at height, (*h*) and the calculated wind run (*u*, m h^{-1}) at that height . The average NH_3 gas horizontal flux (F_h) (mg NH_3-N m^{-1} h^{-1}) for that layer (h_n-h_{n-1}, m) was obtained by the modified equation (Eq.7.1)

$$F_h = u * C \qquad \text{(Eq.7.11)}$$

The wind run was measured at 3.5 m above ground level was calculated by Eq.7.2 to predict the wind run profile for each of the 6 layers ($h_1 - h_6$).

$$u_{h_n} = u_{3.5m}\,(Aln(h_n) + B) \qquad \text{(Eq.7.2)}$$

The constant A and B are specific to pasture surfaces and are derived from (Ryden and Mcneill 1984).The estimated total flux of NH_3 was calculated using the measured NH_3 concentration and the predicted wind run for each layer. The net total horizontal flux (F_v, (mg NH_3-N m^{-2} h^{-1}) was calculated by

$$F_V = \frac{1}{\mathrm{x}}\sum_{h=1}^{h=6}(F_h)\Delta h \qquad \text{(Eq.7.3)}$$

where x = fetch distance (m), h_1 to h_6 shows number of measuring of heights, Δh(m) is the height interval, F_h is the horizontal flux. The total flux (NH_3-N mg h^{-1}) from the pond source area was calculated by multiplying the total horizontal flux (*Fv*, (mg NH_3-N m^{-2} h^{-1}) by the surface area of the pond (m^2)

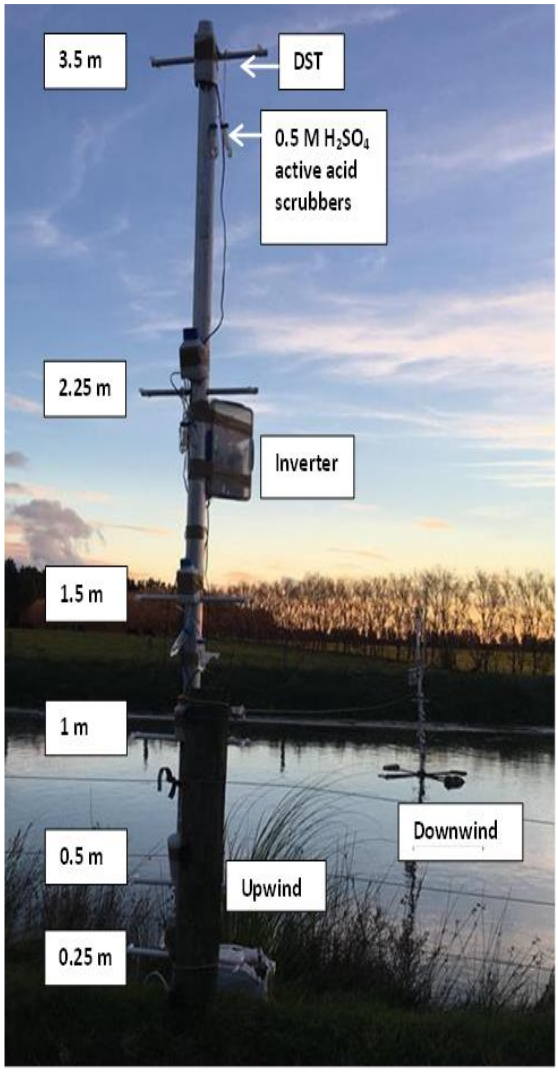


Figure 7. 2: Field set up showing active acid scrubbers and DST mounted at various heights placed at upwind and downwind edge of the pond to integrate horizontal flux coupled with weather station to record wind speed and wind direction.

The pond is not circular therefore the masts were positioned at north, east, south and west banks of the pond. The masts are positioned to isolate the source of NH_3 gas emissions. Back ground upwind concentrations were negligible and were eliminated from the calculation. Mostly, the measurements are made over a time period of (48 h - 96 h) which allows the concentrations recorded at each mast to be summed up for a particular measurement time period. Fetch distances from each measurement mast across the pond were measured at 15 degrees intervals on scaled layout of the pond (Figure 7.3). For each point wind run and fetch will be different because over a period of time wind direction changes which will also change fetch distance therefore it's important to know how much wind run passed through a fetch for each wind run. For the North mast, when the wind is coming from N any angles below 90 and above 170 no wind passes over the source

therefore the source fetch for any wind coming from those directions will also be zero. Similarly for the East mast any wind coming from 0 to 180 degrees will not pass over the pond because that area is adjacent to the barn which restricts the airflow. For example, the figure 7.3 clearly shows how fetch varies as we change the orientation of masts. The dotted lines show the possible fetch distances as measured from each mast at 15 degrees interval. The figure presents an example of a period with wind direction from 120 degrees for the N mast and at 105 degrees for E mast therefore the fetches across the source are zero for N and E masts. For the same period the South and West mast the fetch distance at 15 degrees are 63.1 m and 31.3m respectively. The fetch distances were converted to meters by using the diagrams scale factor (1 cm = 4.67m). At the end of each sampling period total wind run was summed up based on the sampling start and end time.

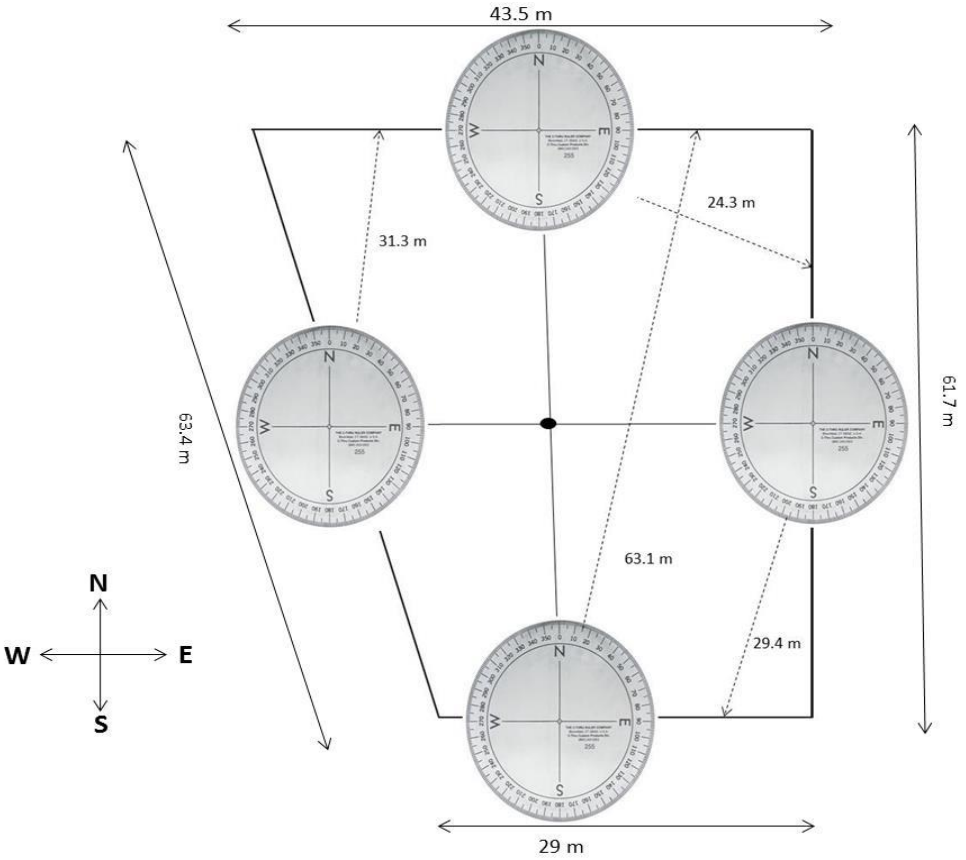


Figure 7. 3: Lay out of the field set up showing DSTs, at the centre of each compass mounted at various heights placed at North, East, South and West edges of the pond to integrate horizontal flux coupled with weather station to record wind run and wind direction

7.2.3 Micrometeorological data

A full set of weather data was recorded for experimental period using weather station model XC03069 mounted at N end of the pond.

7.2.4 Daily evaporation rate (ETR)

The weather data and soil moisture records were used to construct a soil water balance model (Bretherton et al., 2018). Pan evaporation estimates calculated by this model were used to estimate pond evaporation rates and test the relationship between evaporation and NH_3 volatilization rate off the storage pond.

7.2.5 Slurry collection and Nutrient analysis

Raw slurry samples were collected from the top surface (1 – 10 cm) on the days when gas emission flux measurements were recorded to study the spatial and temporal variation in the slurry chemical properties. After collection fresh slurry samples were brought back to laboratory for pH and DM content analysis and kept frozen at -18 ºC if the nutrient analysis wasn't done on the same day. Slurry sub-samples were analyzed for total ammoniacal N (TAN), totak Kjeldahl N (TKN), total Kjeldahl P (TKP). The extraction details have been given section 4.2.2 of Chapter 4.

7.2.6 Statistical Analysis

Multiple linear regressions was performed with MS office Excel 2013 to study the relationship between daily ET rate, slurry TAN, pH and NH_3 emission flux to predict and estimate N losses based on these parameters.

7.3 Results

7.3.1 Meteorological data

For both measurement periods the weather was moist and cold (mean temps 5º C – 10 ºC) during the experiment with several rainfall events.

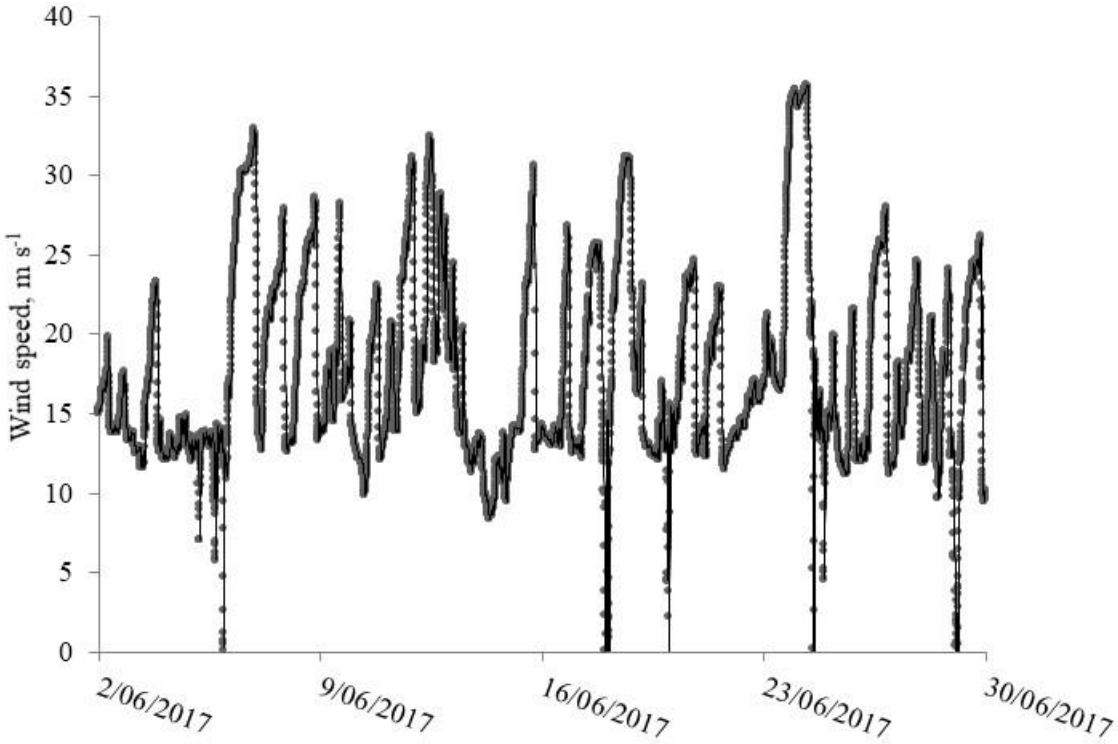


Figure 7. 4: Trend in wind speed (averaged every 5 minutes) in June, 2017

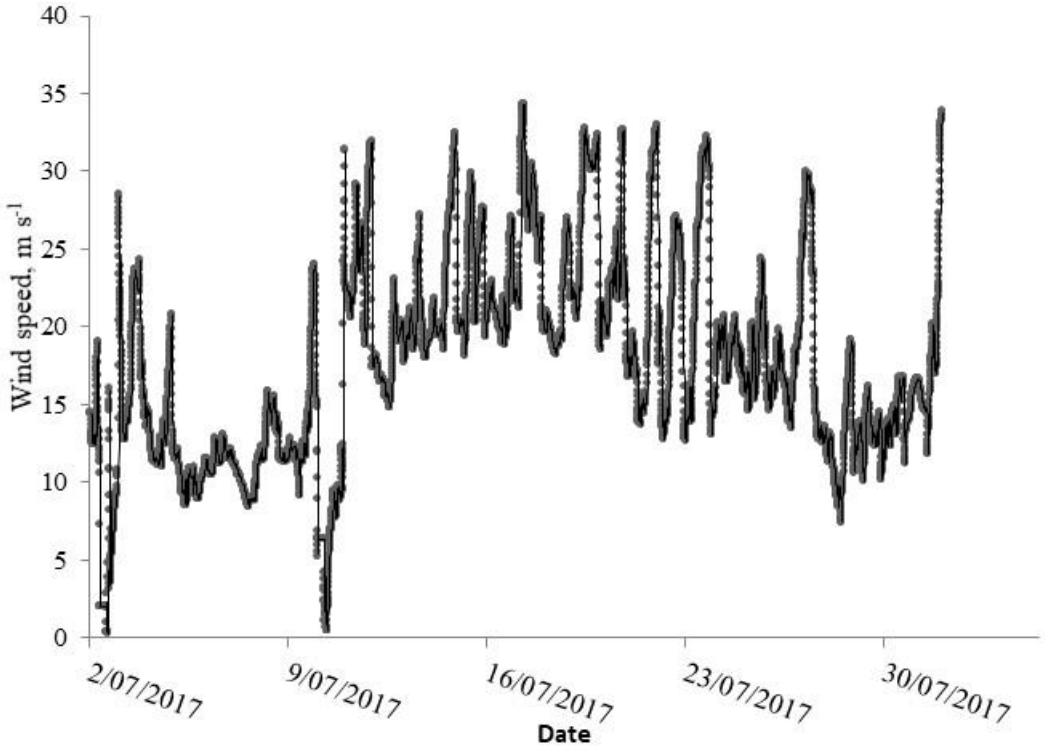


Figure 7. 5: Trend in wind speed (averaged every 5 minutes) in July, 2017

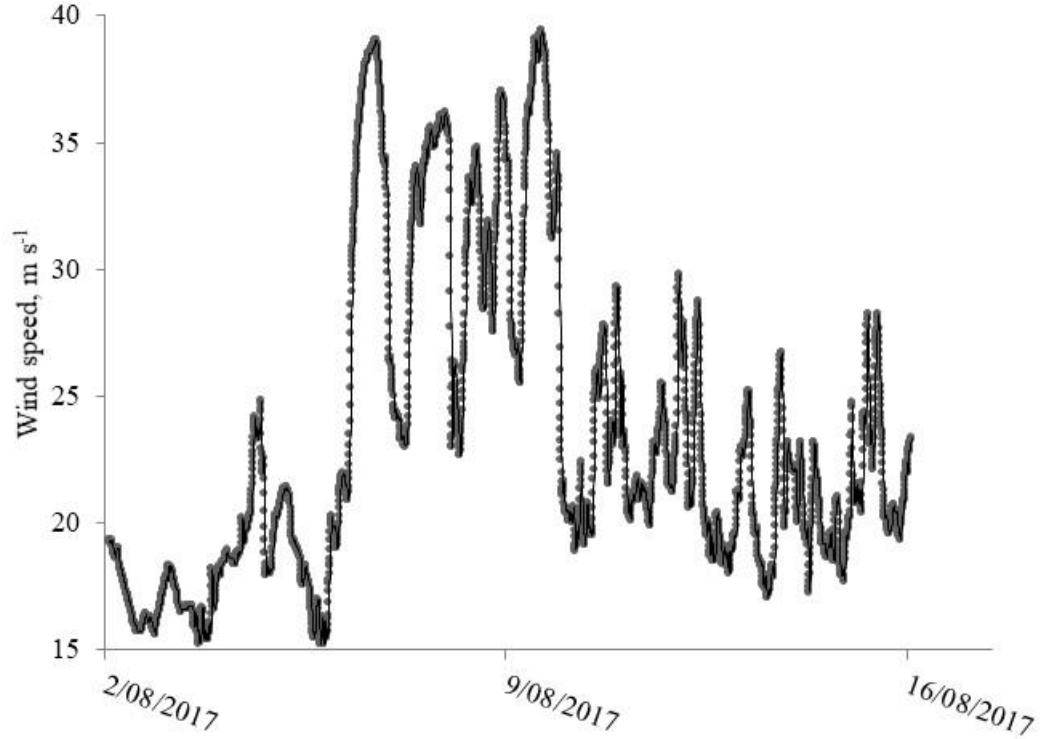


Figure 7. 6: Trend in wind speed (averaged every 5 minutes) in August, 2017

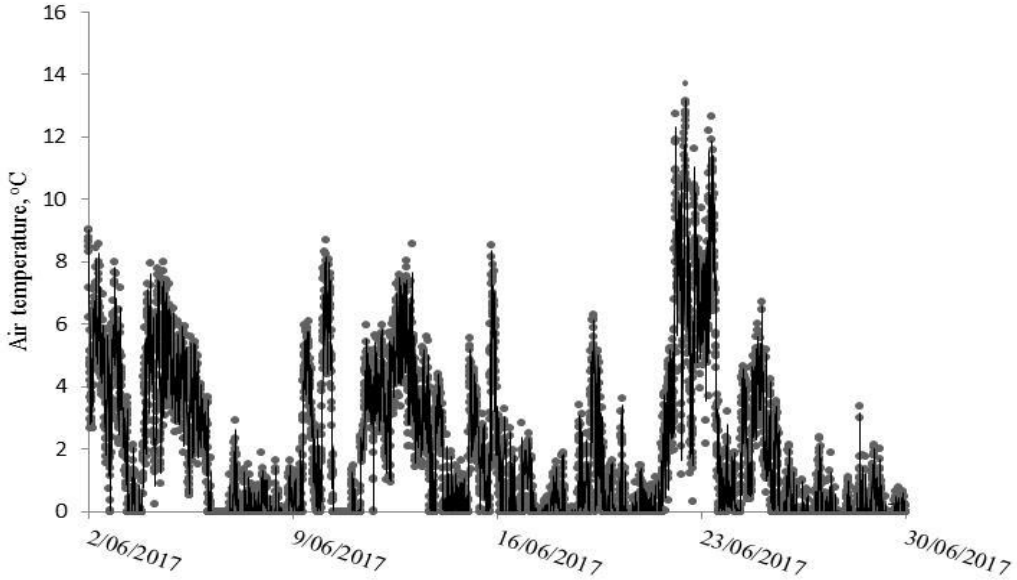


Figure 7. 7: Trend in air temperature (averaged every 5 minutes) in June, 2017

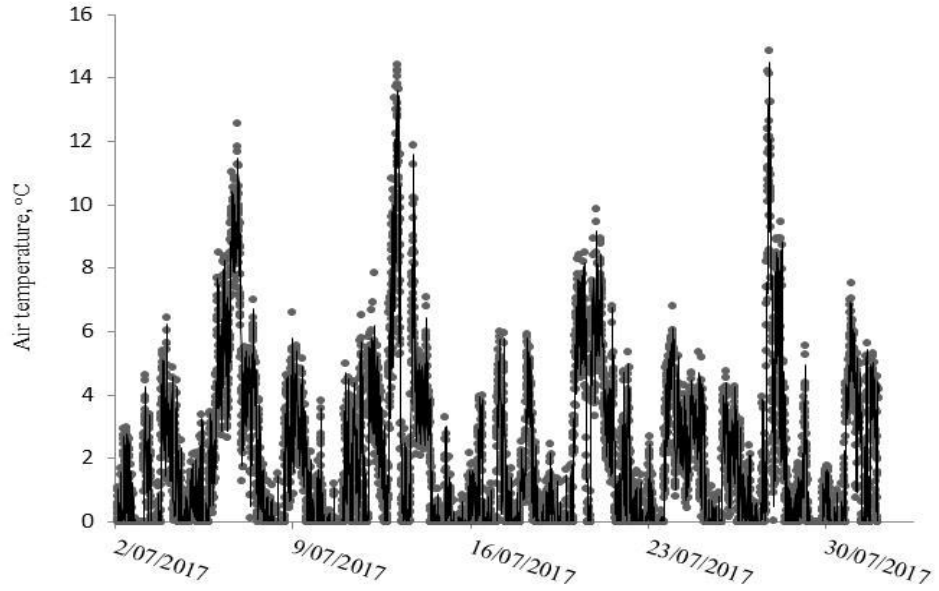


Figure 7. 8: Trend in air temperature (averaged every 5 minutes) in July, 2017

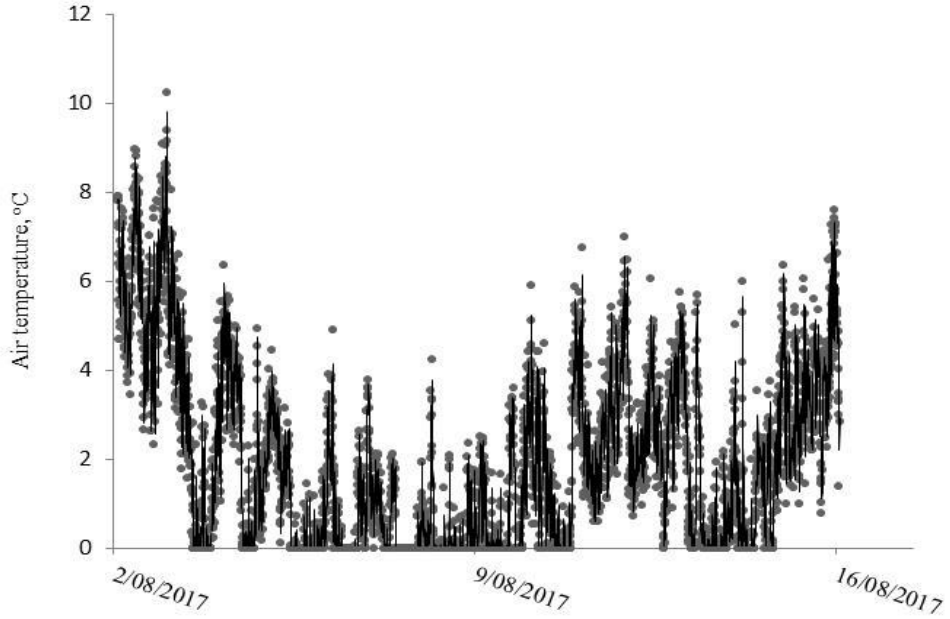


Figure 7. 9: Trend in air temperature (averaged every 5 minutes) in August, 2017

The wind speed ranged between 0 m s^{-1} and 13.7 m s^{-1} and averaged 1.8 m s^{-1} in June (Figure 7.4), between 0 m s^{-1} and 14.9 m s^{-1} and averaged 2 m s^{-1} in July (Figure 7.5) and between 0 m s^{-1} and 10.2 m s^{-1} and averaged 1.9 m s^{-1} in August (Figure 7.6). Similarly, the air temperature ranged from 0 ºC and 16.4 ºC and averaged 16.4 ºC in June (Figure

7.7), 0 ºC and 17.4 ºC and averaged 17.6 ºC in July (Figure 7.8) and 15.2 ºC and 39.4 ºC and averaged 23.4 ºC in August (Figure 7.9).

7.3.2 Calibration of DSTs to calculate the NH_3 gas concentration in the air

Please refer to Section 3.5.2.1 of Chapter 3 for all the details.

7.3.3 Wind run

Wind run was calculated as the sum of the total air passed over the storage pond corresponding to the fetch over periods of 24, 48, 72 and 96 hours at every 30 degrees interval. The total wind run (m) at each height was calculated instead of integrating wind speed (m s^{-1}). The Figure 7.10 presents an example of wind radar diagram for integrating wind run over 96 hours. In the Figure 7.10 (a) the wind direction is uniform dominated by EES whereas in the Figure 7.10 (b) the wind run is scattered coming from E, EES and SES.

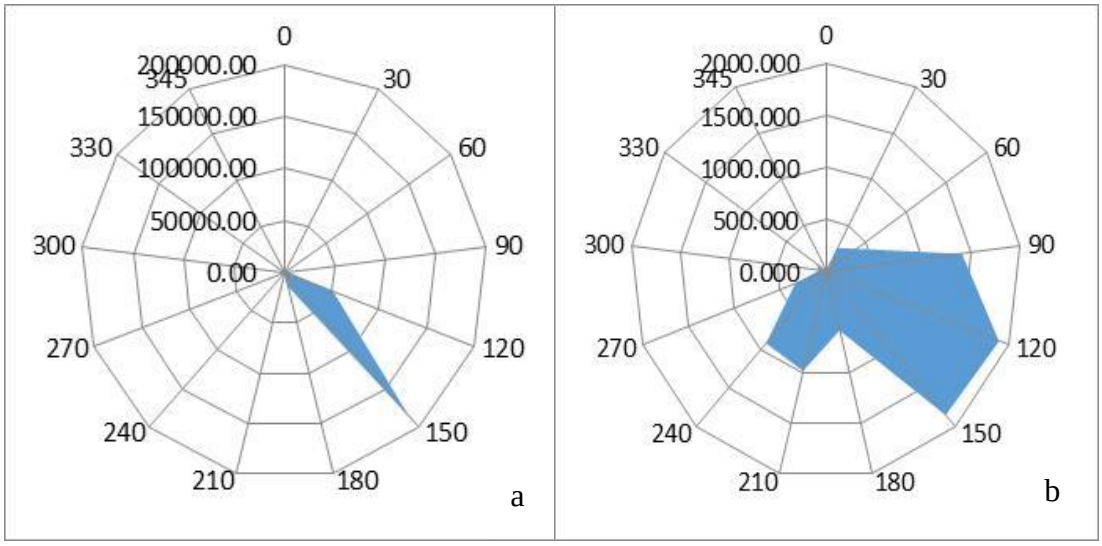


Figure 7. 10: The wind run (m) and wind direction frequency distribution on radar chart over 24 (a) and 48 hours (b) summed at 30 degrees interval

7.3.4 Slurry chemical characteristics

The trend in slurry pH and concentrations of total Kjeldahl nitrogen (TKN), total Kjeldahl phosphorus (TKP) and total ammoniacal contenct (TAN) in slurry samples collected from the top 1 - 10 cm of the slurry pond are presented in Figures 7.11 and 7.12. The concentration of TAN content in slurry ranged from 218 - 360 mg L^{-1} and averaged 305

mg L^{-1}, TKN concentrations ranged from 308 - 519 mg L^{-1} and averaged 443 mg L^{-1} whereas TKP ranged from 38 - 85 mg L^{-1} and averaged at 67 mg L^{-1}. The pH of slurry ranged from 7.67 - 7.98 measured over a period of time (Figure 7.11). Nutrient concentration reported here are similar to (Chrystal et al. 2016; Longhurst et al. 2017) when the samples were collected from a static pond. The %DM content of slurry samples ranged from 0.2 - 0.4%. The nutrient concentrations in liquid and solid effluents collected from various farming practices in NZ and attributed the variability in nutrient concentrations to mainly to management practices at the farm (Chrystal et al. 2016; Longhurst et al. 2017).

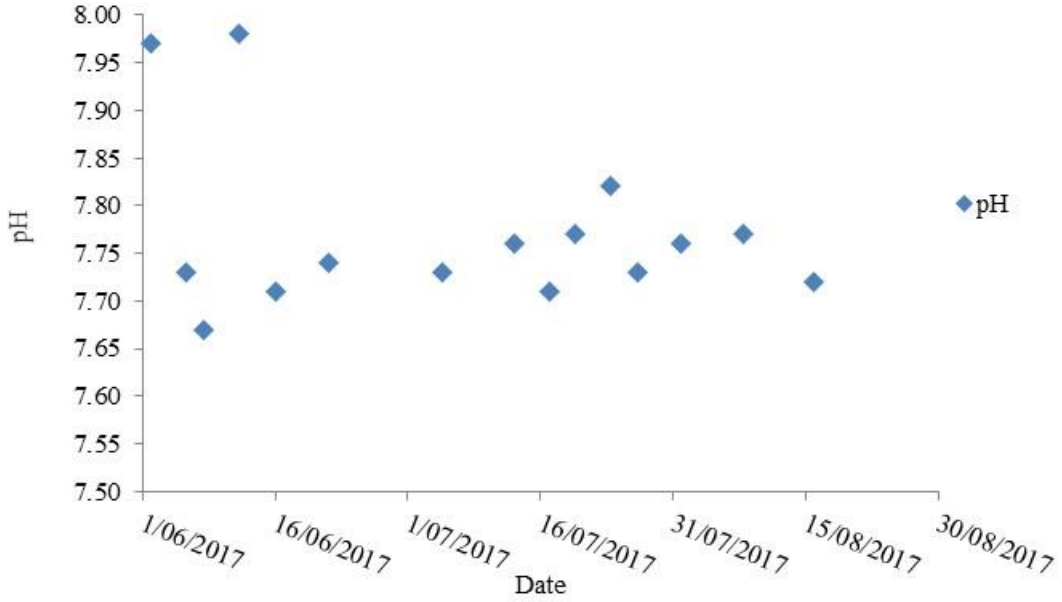


Figure 7. 11: Trend in slurry pH in top 1 - 10 cm of pond surface measured over 2nd June - 16th Aug, 2017

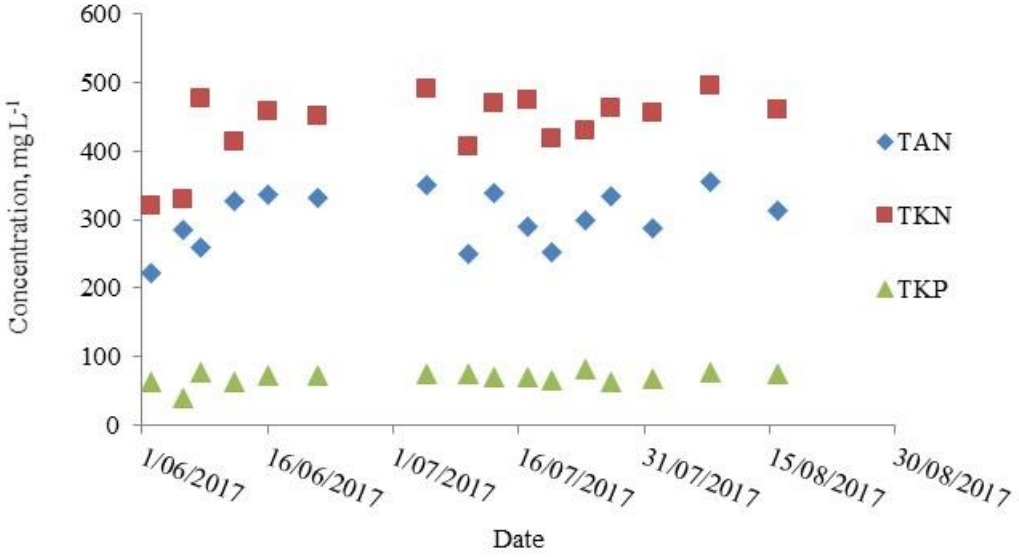


Figure 7. 12: Trend in slurry TAN (mg N L^{-1}) , TKN (mg N L^{-1}) and TKP (mg P L^{-1}) in top 1 - 10 cm of pond surface measured over 2nd June - 16th Aug, 2017

7.3.5 Correlations of ammonia emissions, slurry characteristics and ET rate

It was observed that on days when the ET rate was high the emission flux was also high and vice versa. Figure 7.13 shows the pan ET rate and NH_3 emission flux (averaged for a sampling duration) measured from the top surface of the slurry pond.

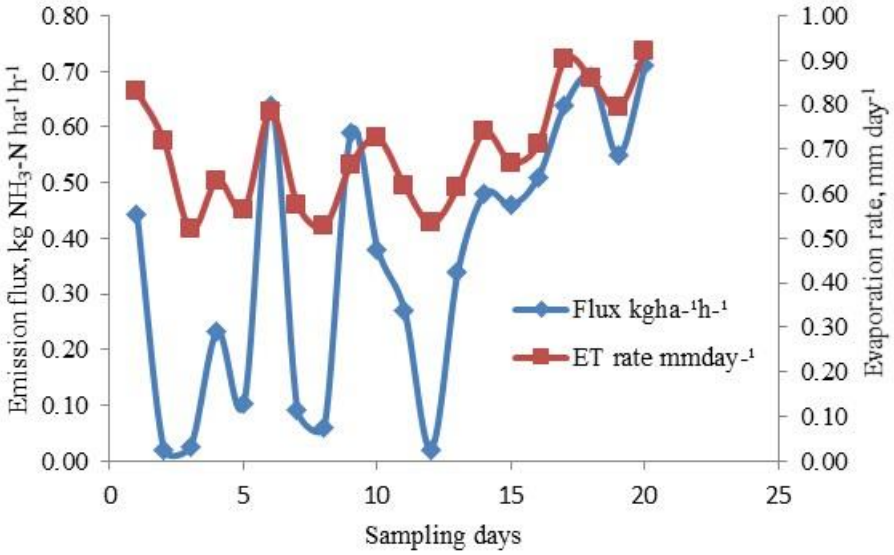


Figure 7. 13: Rate of NH_3 emission flux (kg NH_3-N ha^{-1} h^{-1}) and daily evaporation (mm day^{-1}) measured over 2nd June - 16th Aug, 2017

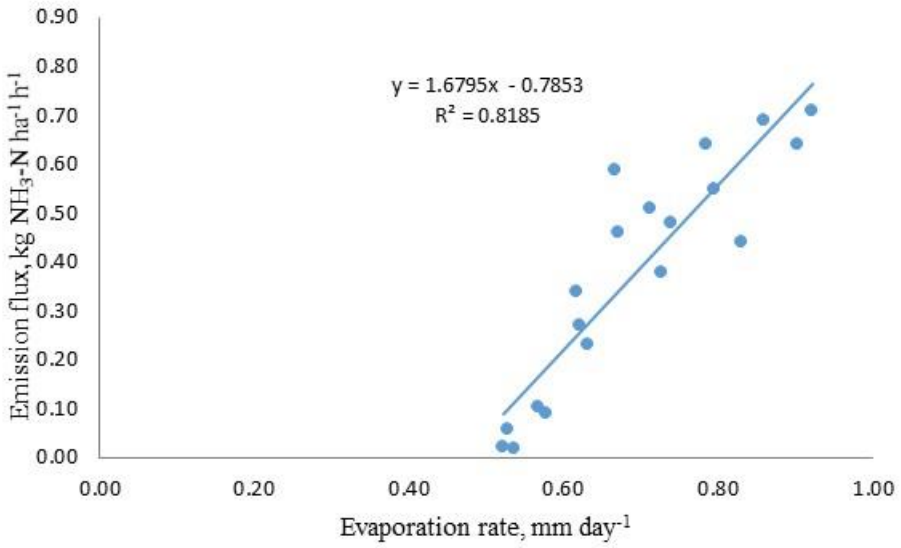


Figure 7. 14: Relationship between observed NH_3 emission flux (kg NH_3-N ha^{-1} h^{-1}) and ET rate (mm day^{-1}) measured over 2nd June - 16th Aug, 2017

The results of simple linear regression between pan ET and emission flux (R^2 = 0.81) showed a strong positive relationship between two parameters (Figure 7.14). According to (Sommer and Husted 1995) slurry pH, TAN content and atmospheric conditions are the most important factors controlling the release of NH_3 gas form slurry during storage. Similarly, many other studies have also reported that release of NH_3 gas during slurry storage are influenced by atmospheric conditions and slurry characteristics with (Amon et al. 2006; Leytem et al. 2013; Page et al. 2014; Sun et al. 2014). Therefore, the above correlations were further explored by using these two components averaged (NH_3 gas emission flux and ET rate) along with slurry pH and TAN concentrations in the slurry to build a model to predict NH_3 losses from the surface of storage pond (Table 7.1)

Table 7. 1: Daily ET rate from the pond, NH_3 emission flux, pH and TAN concentration in slurry to predict NH_3 losses measured over 2/06/2017 - 16/08/2017

Sampling #	Ammonia emission flux kg ha^{-1} h^{-1}	TAN kg L^{-1}	pH	Average ETR mm day^{-1}	Predicted flux kg ha^{-1} h^{-1}
1	0.44	0.000273	7.97	0.83	0.5
2	0.02	0.000256	7.73	0.68	0.1
3	0.02	0.000317	7.67	0.52	0.1
4	0.23	0.000325	7.70	0.63	0.3

5	0.10	0.000317	7.68	0.57	0.2
6	0.64	0.000327	7.72	0.78	0.5
7	0.09	0.000327	7.64	0.58	0.2
8	0.06	0.000332	7.77	0.53	0.2
9	0.59	0.000337	7.85	0.67	0.5
10	0.38	0.000282	7.82	0.73	0.3
11	0.27	0.000271	7.77	0.62	0.1
12	0.02	0.000277	7.72	0.54	0.0
13	0.34	0.000321	7.69	0.62	0.2
14	0.48	0.000321	7.74	0.74	0.4
15	0.46	0.000336	7.71	0.67	0.4
16	0.51	0.000336	7.75	0.71	0.5
17	0.64	0.000322	7.81	0.90	0.7
18	0.69	0.000335	7.86	0.86	0.7
19	0.55	0.000321	7.82	0.79	0.6
20	0.71	0.000333	7.91	0.92	0.8

The above data was used to determine the relationship between the measured NH_3 emissions flux against pH and TAN (Table 7.2). It is important to maintain that ET rates expressed in mm day^{-1} are equivalent to kg^{-1} ha h^{-1}.

Table 7. 2: Table of coefficients of the model to predicted NH_3 flux (kg N ha^{-1} h^{-1}) as a function of measured pH and TAN and ET

Factors	Coefficients	SE	t stat	P value	R^2
Average pH	0.54	0.469	1.16	0.263	0.86
Average TAN	3244.03	987.96	3.28	0.005	
Average ET	1.38	0.28	4.89	0.0001	
Intercept	-5.84	3.53	-1.65	0.119	

1predicted NH_3 = 0.54pH+3244.03TAN+1.38ET-5.84

From multiple linear regression models, pH, TAN and ET rates were found very useful in predicting NH_3-N losses. Figure 7.15 shows strong and positive relationship between

observed and predicted NH_3 emission flux. The model (Table 7.2 and Figure 7.15) explains 86% of the variation in NH_3 flux (R^2 = 0.86). The results show that the concentration of TAN in the top surface slurry does not alter much over a period of time indicating that the only dominant factor influencing the NH_3 emission flux would be the daily ET rate. A threefold increase in nutrient concentrations (TAN and TKN) was observed when the slurry samples were collected after mechanically agitating the pond slurry before land application Chapter 8; Table 8.3. The impact of change in TAN concentrations on NH_3 emission flux is further explored explained and in next chapter. These results were consistent with (Amon et al. 2006; Leytem et al. 2013; Page et al. 2014; Sun et al. 2014) who also found that evaporative losses explain the variations in emission flux.

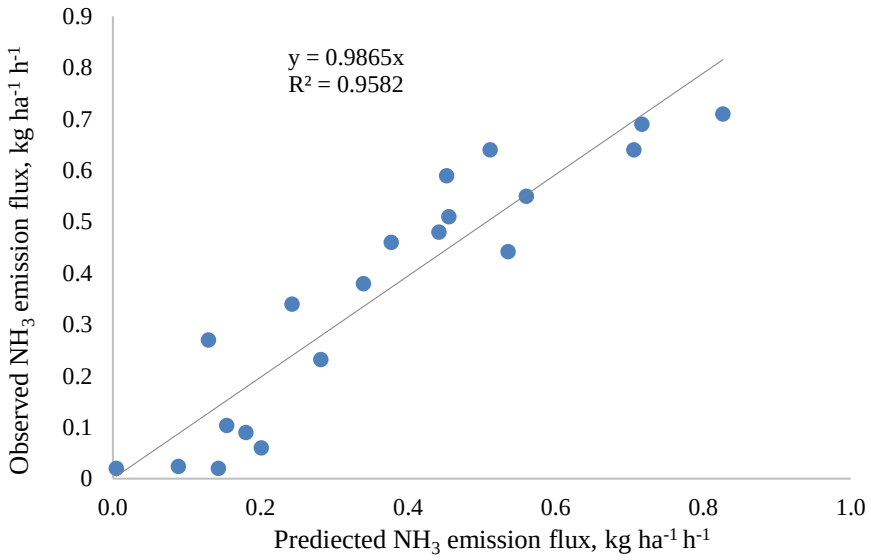


Figure 7. 15: Relationship between observed and predicted NH_3 emission flux obtained using the equation NH_3 flux (kg N ha^{-1} h^{-1}) = 0.54pH+3244.03TAN+1.38ET-5.84

7.6 General Discussion

This chapter explores the convenient and inexpensive technique for monitoring NH_3 losses off the slurry storage pond along with atmospheric and slurry characteristics driving NH_3 emissions. The modified IHF flux technique using DSTs provide simple and cost effective long-term emission measurements. Simplifying the flux calculations by integrating wind run instead of wind velocity eliminates complicated and long calculations. During slurry storage pH elevation and TAN [NH_3+NH_4^+] is due to the conversion of organic N into and inorganic form which increases alkalinity hence high

pH (Sommer et al. 2006). The release of CO_2 and NH_3 from the surface of storage pond also elevates pH over time which further accelerates the emission of NH_3 gas to the atmosphere (Blanes-Vidal, Sommer, and Nadimi 2009). The high pH of slurry during storage has been attributed to microbial activity, release of NH_3 and CO_2 and decrease in acetic acids (Blanes-Vidal et al. 2009; Petersen et al. 2012), low concentration of volatile fatty acids (VFAs) and degradation of organic compounds in the slurry (Eriksen, Peter, and Lars 2008). Petersen et al. (2012) observed an increase in pH from 7 to 7.5 from untreated dairy cattle manure. The only pilot scale study in NZ compares and measures the gaseous NH_3 emissions from manure collected from two different manure storage practices (weeping walls vs storage bunkers) on a pilot scale using chambers over 4 months (van der Weerden et al. 2014). The authors found the impact of slurry characteristics like total solid content, TAN and TKN content and C : N ratio but the impact of environmental factors wasn't studied. Our study provides an overview of different climatic and manure characteristics driving NH_3 emissions. The relationship between slurry characteristics and atmospherics parameters also confirm the suggestions of (Laubach et al. 2015), the authors emphasized on the influence of pH, slurry TAN content, wind and temperature on magnitude of NH_3 volatilization. These parameters could be very useful in estimating NH_3 losses from a slurry storage pond, given the similar weather conditions NH_3 losses are expected to be similar to the results reported but more widespread monitoring is required in NZ.

For the Massey Barn slurry storage pond the relationship NH_3 flux (kg N ha^{-1} h^{-1}) =0.54pH+3244.03TAN+1.38ET-5.84 was used to predict NH_3 loss from weather records for the period 25/07/2016 to 15/10/2016. It was assumed that the pH and TAN were similar to the average measurements made in June to August, 2017. If effluent had to be stored for 30, 60 and 90 days starting in June 2016 the cumulative NH_3 losses would be 13 kg NH_3-N ha^{-1}, 36 kg NH_3-N ha^{-1} and 1104 kg NH_3-N ha^{-1} respectively.

7.7 Summary and conclusions

NH_3 emissions from slurry storage were monitored and measured using a cheap and reliable technique. The impact of atmospheric factors such as daily evaporation rate from the top surface of pond and slurry characteristics such as pH and TAN influencing NH_3

emissions were studied and then a simple model using these parameters was developed to predict NH_3-N losses from slurry storage pond. Based on these factors the following conclusions were drawn:

- NH_3 emissions can be effectively monitored over long term using improved IHF methodology
- Chemical characteristics of slurry like pH and TAN and atmospheric parameters such as daily ET rate are important factors in driving NH_3 emissions.
- Local NZ Metservice data for ET and regular measurements of slurry pH and TAN can provide a simple method for predicting NH_3 loss from storage ponds.
- Pond agitation has an impact on changing chemical characteristics of the slurry and these pH and TAN values should not be used to predict NH_3 loss from unmixed (static) storage ponds
- The magnitude of NH_3 emissions from the storage pond depends on the duration of manure storage.
- The longer the durartion of the storage (3 months or more) the higher will be the kg NH_3-N lossed from the pond.
- Strategically emptying the pond slurry and its reapplication back to paddocks could help minimising N losses off the pond.

Chapter 8

Measurement of ammonia volatilization from freestall barn holding-pond slurry re-application to land through surface spray and injection

8.1 Introduction

Land application of holding-pond slurry or farm dairy effluent (FDE) back to the farm is the final stage of manure management chain common to NZ dairy farms. The animal excreta contains important nutrients which will reduce the need for purchased fertiliser and enhance soil fertility and N utilization efficiency of the whole farming system. The composition of slurries vary with source, such as farm dairy effluent, or feed pad and barn effluents (Longhurst, Roberts, and O 'connor 2000). Feeding practices, and the practices used for handling, storage and reapplication of the effluent or slurry can impact strongly on NH_3 volatilization loss (Li et al. 2015). The timing and method of application of slurry also is important to conserve the nutrient content in manure (Huijsmans et al. 2003). Different types of manure destined for land application have different impacts on NH_3 volatilization because of differences in TAN, pH, DM content and other chemical properties. For example cattle slurry with a high dry matter content will infiltrate less in soil and volatilize NH_3 rapidly (Stevens and Logan 1987; Thompson, Pain, and Rees 1990). Dairy cattle slurry has high dry matter content and less infiltration capacity than pig slurry (Misselbrook et al. 2005a).

There are three main techniques of manure application (band spreading, injection and broadcast spread). NH_3 emissions can be minimised by using appropriate manure application techniques, the losses have been reported to be reduced by rapid infiltration/injection of slurries into recently tilled soil because of its high capacity to absorb slurry. Many overseas studies have been conducted to compare and quantify the volatilization losses following slurry application but in NZ, limited numbers of studies have been conducted on measuring NH_3 emissions from re-application of manure, specifically FDE, to permanent pasture. Many of these studies conducted on FDE application (Di et al. 1998; Houlbrooke et al. 2004) have been focussed on quantifying

nutrient content, and application techniques that reduce, nitrate losses to water. The research has been summarised in a guide for farmers (A farmer's guide to managing farm dairy effluent – DairyNZ 2015). Li et al. (2015) have reviewed the research techniques to reduce the losses of all N gases on the reapplication of farm dairy effluents to land. Much of the focus of previous research was to reduce N losses to water and atmosphere by varying irrigation rate and the use of nitrification and urease inhibitors. There is currently a lack of information on NH_3 losses from the reapplication of stored free-stall barn manure to pasture and standoff pad effluent. Most studies have reported the impact of application technique on NH_3 volatilisation, the literature relying mostly on the experiences of researchers in the US (Hristov et al. 2011; Holly et al. 2017; Sun et al. 2014) and EU (Huijsmans et al. 2003; Webb et al. 2010, 2014) where applications are often made to cultivated cropland and not permanent pastures . The main objective of this study was to compare the scale of NH_3 volatilization losses upon application with those of the other stages of manure handling reported in previous Chapters. This study also compares two different techniques (tanker spray and trailing shoe injection) of stored pond effluent applied to land (grazed pastures) and their effect on NH_3 volatilization loss.

8.2 Materials and Methods

8.2.1 Experimental Site

Two separate applications and measurements were carried out in late spring-early summer (November, 2015) and early autumn (April, 2016). The experiment was carried out on Massey University's Dairy No. 4 farm near Palmerston North, Manawatu, New Zealand (40^o 23' 46.79" S; 175^o 36' 35.77" E). The farm has 98 paddocks and experiments were performed on two of these paddocks with an average area of ca. 2.3 ha. The paddock has flat topography (c. <3% slope) with an annual rainfall ca. 1000 mm. The soil in the paddock is Tokomaru silt loam, which is classified as an Argillic-fragic Perch-gley Pallic Soil (Hewiit 2010). A detailed description of soil physical properties is provided by Scotter et al. (1979). The soil is naturally poorly drained and consists of a weakly to moderately developed brown, silt loam A horizon to a depth of 250 mm. There is a weakly developed, grey, strongly mottled, clay loam B horizon to 800 mm and a C horizon of highly compacted, pale grey, silt loam fragipan, which acts as a natural barrier

to drainage. The paddock is mole and pipe drained, and grows a mixed sward of perennial ryegrass (*Lolium perenne)* and white clover (*Trifolium repens*).

Figure 8. 1: An aerial view of the trail site on the day of manure application (trial 1) showing location of the barn, storage pond and application of the slurry using commercial tankers (Google Earth, Nov, 2015)

8.2.3 Soil tests for soil fertility

The plots used for the slurry application were part of the duration-controlled grazing study conducted by Christensen (2013). The previous history of freestall barn slurry applications to the duration controlled plots has been document by Christensen (2013). Soil tests undertaken by Christensen (2013) are presented in Table 8.1.

Table 8. 1: Soil test mean results for duration controlled grazing plots at the trial site from (Christensen, 2013)

pH	Olsen P ($\mu g\ g^{-1}$ soil)	Sulphate S ($\mu g\ g^{-1}$ soil)	QT K	QT Ca	QT Mg
5.7	37.1	34.3	4.4	8.3	27.8

8.2.4 Weather conditions

A full set of weather data was recorded for each of the summer and autumn applications. For both applications the weather was sunny and dry (mean temperature 14 ºC – 17 ºC) before and during the experiment and no rainfall had occurred. Wind speed and direction

was recorded using 3D sonic anemometer. Wind speed (m s^{-1}), wind direction (º), air temperature (ºC) were recorded every 10 seconds by a 3D sonic anemometer placed beside the measuring masts. At the end of the experiment, wind speed, wind direction and air temperature were averaged over five minute intervals to be reported for the 32 hours of measurement period.

8.2.5 Soil water balance

The weather data and soil moisture records were used to construct a soil water balance model (Bretherton et al. 2018). This was used to estimate soil-limited evapotranspiration rates and test the relationship between soil limited evapotranspiration and NH_3 volatilization (see also Chapter 7) following slurry re-application to land.

8.2.6 Slurry application techniques

The slurry used for land application was obtained from the pond used for storing slurry from the free-stall barn (described in Chapter 7). The barn flooring is concrete therefore the slurry is a mixture of urine, dung and rain water only as the storage pond is not covered. Before the re-application of slurry to the designated plots, slurry was thoroughly stirred with a commercial stirrer with high pressure jets so that the slurry is well-mixed and can easily be sucked through the hoses connected to the tankers for applying it to the paddocks. Two slurry application techniques surface spray and injection were used to compare NH_3 volatilization losses off the land application trial. Surface spray was carried out using commercial application tankers a Williams 'Elephant 5000' slurry tanker with specific hoses and fittings for slurry spray and 'Solodisc injector system' with 24 trailing shoe injectors for injecting slurry into the paddock (Figure 8.2). The discs openers are used in conjunction with hoe coulters to inject through the pasture and slurry is dispensed directly into soil. The hoe coulters are 21.5 cm apart from each other. For trial 1, summer application, the slurry application rate for surface spray was 98 $m^3\,ha^{-1}$ (2.74 ha) and for injection was 111 $m^3\,ha^{-1}$ (0.8 ha) whereas trial 2 in autumn, the application rate for slurry surface spray 107 $m^3\,ha^{-1}$ (2.98 ha) and injection was 98 $m^3\,ha^{-1}$ (2.48 ha) respectively. For trial 1 the application was made at 10 am in the morning on 5th November, 2015 and for the autumn application, slurry was applied at 12 pm noon on 27th April, 2016.

Figure 8. 2: Slurry application to land using commercial tankers for surface spray using a Williams 'Elephant 5000' slurry tanker and 'Solodisc Injector system' for injecting slurry into the land

8.2.7 Ammonia volatilization measurements

Ammonia emissions following the slurry application were measured in the paddock on two occasions using micrometeorological mass balance and integrated horizontal flux methodology (Denmead et al. 1998; Ryden and Mcneill 1984) coupled with 3D sonic anemometer. The active gas sampling technique has been described in detail in Chapter 3 and Chapter 7 of this thesis however; the only difference is that of the gas sampling heights. The downwind and upwind boundaries were defined based on the wind direction forecast from MetService (https://www.metservice.com/rural/manawatu), where the masts were positioned with 10 ml H_2SO_4 acid traps contained in 50 ml poly propylene centrifuge tubes at 0.25 m, 0.5 m, 1.5 m and 2.25 m above the ground level (Figure 8.3). Traditionally circular plots are used for IHF methodology to make it independent of wind direction but in this experiments the orientation of the masts along the downwind and upwind boundaries of the plot were changed based on the wind direction forecast on the measured site. The volume of the air (L min^{-1}) pumped through each acid trap was measured with hand held flow meter before and after changing the acid trap. The first trial's measurements were performed between 5th and 7th November, 2015 and the second trial was carried out between 27th and 29th April, 2016. The NH_3 emissions measurements were commenced immediately after the slurry application using a fetch distance of 20m between masts and continued for 48 hours for both trials. Acid traps were changed after 2, 4, 8, 16 and 32 h respectively. This allowed for day and night measurements of NH_3 flux to be separated. The horizontal flux is calculated based on the product of NH_3 gas

concentration in the acid traps (mg m^{-3}) placed at different heights (m) and the wind speed (m s^{-1}). The calculations of NH_3 concentrations and flux have been explained in Chapter 7 section 7.2.3.3; however the only difference was that of integrating wind speed rather than wind run. NH_3 losses were expressed as a % of the nitrogen load applied.

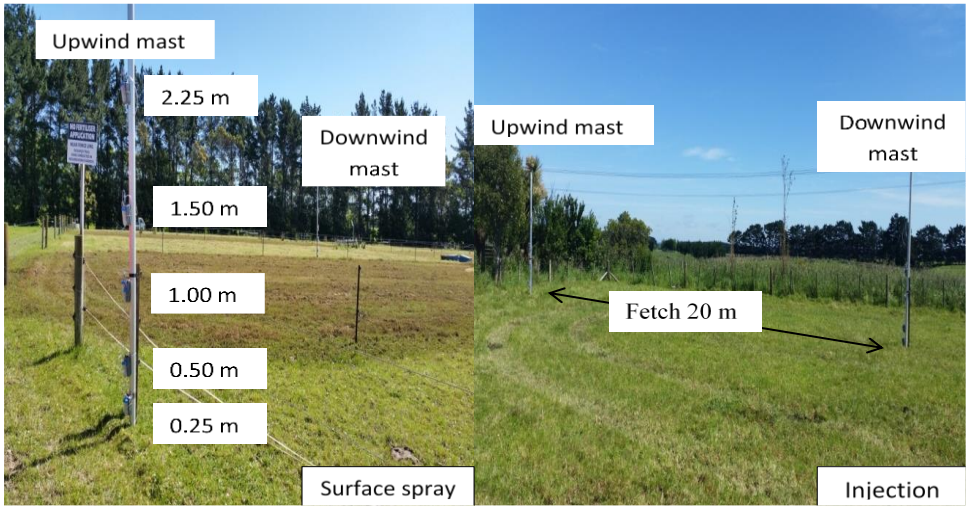


Figure 8. 3: Downwind and upwind set up of masts for measuring NH_3 volatilization losses following slurry application to land using integrated horizontal flux methodology (NH_3 acid traps at 0.25 to 2.25 m above ground

8.3 Results and Discussion

8.3.1. Slurry properties and application rate

The chemical properties of the holding pond slurry are given in Table 8.2. The total N application rates were calculated based on the paddock size and volumes of the slurry applied varied for both applications (Table 8.2). For autumn applications the rate of N applied was 3 fold higher than summer applications. There was a slight difference in DM content of the slurry (% total solids) for the both applications (Table 8.2). The dry matter and N concentrations of the effluents are within the range of concentrations reported for stored pond dairy effluents in NZ (Houlbrooke et al. 2011). According to Houlbrooke et al. (2011) stirring pond-stored, slurry from a wintering barn in South Island effectively produced homogenised mixture. They reported a total N concentration (TKN) of 3190 mg N L^{-1} (0.32% N) and %DM of 8.1 based on the analysis of 3 samples. However, for Manawatu region, the reported % DM content ranged from 0.6 to 1.8% and TKN from 0.02 to 0.07% N (200 - 700 mg N L^{-1}) from the slurry samples collected off weeping wall. DM content of the slurry depends on duration and handling of slurry storage.

Table 8. 2: Characteristics of the dairy cattle holding pond slurry applied to paddocks with surface spray and injection 7/11/2015 - 9/11/2015 and 27/04/2016 - 29/04/2016

Trials	Application technique	Paddock Size ha	Total solids % DM	pH	NH_4^+-N mg L^{-1*}	NO_3^--N mg L^{-1**}	Total N mgL^{-1*}	Rate of N applied kg N ha^{-1*}
Trail 1	Spray	0.80	0.4	7.71	373	10	734	81
	Injection	2.70		7.71	357	10	747	73
Trial 2	Spray	2.98	0.6	7.29	728	10	2350	252
	Injection	2.48		7.29	684	11	2368	233

*Amount calculated based on the paddock size

**detection level of the colorimetric analysis

8.3.2.1 Trial 1 Summer: Meteorological data

For summer application, the wind speed ranged between 0.58 m s^{-1} and 4.13 m s^{-1} and averaged 2.37 m s^{-1} for the experimental period (Figure 8.4). Day time temperature peaked at 17.4 ºC and the night time low temperature was 7.9 ºC, over-all temperature averaged at 12.9 ºC for the early summer application period (Figure 8.5). It is important to mention that day length was longer for summer application as compared to autumn application. Higher wind speed and higher air temperature were recorded during the day.

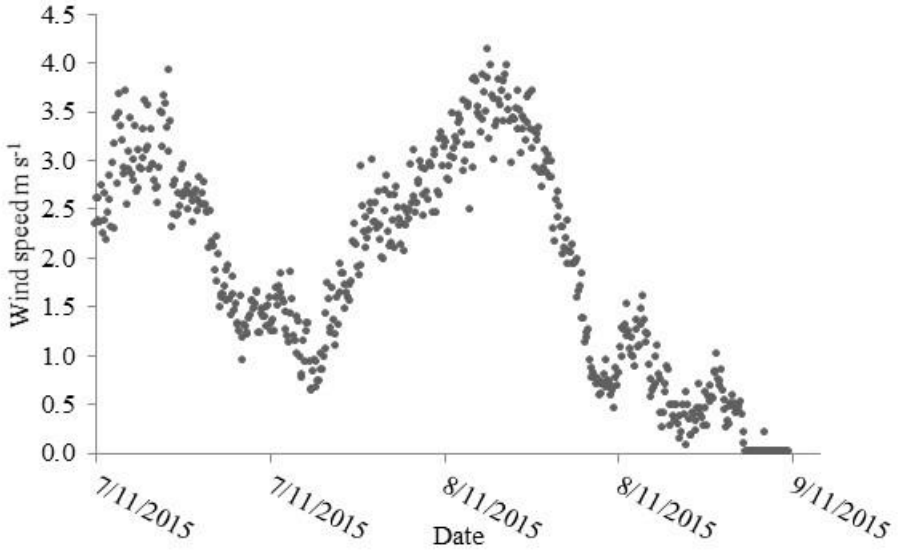


Figure 8. 4: Trend in wind speed (averaged every 5 minutes) over the experimental period: Summer application

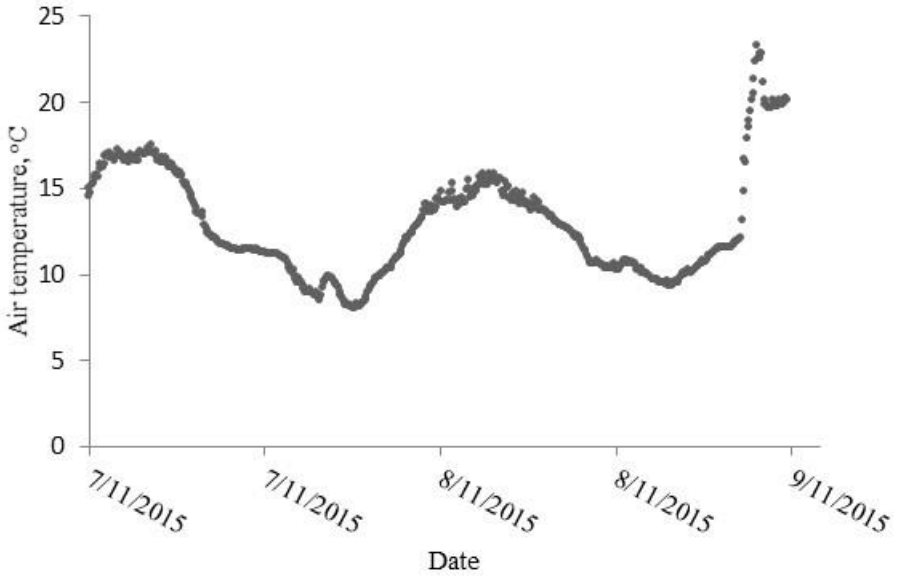


Figure 8. 5: Trend in air temperature (averaged every 5 minutes) over the experimental period: Summer application

8.3.2.2 Trial 1 Summer: Measured ammonia gas concentrations

The NH_3 gas emission profile in the air (difference between the measured NH_3 concentration measured each height at the upwind and downwind boundaries of the paddocks) are shown in Figure 8.6 and 8.7. The gas concentrations measured at upwind edges of the paddocks were used to estimate the background concentrations of gas. The profiles of NH_3 gas concentration in the air at each height showed that the gas concentration measured at 0.25 m above ground was at least 3 times higher than measured at 2.25 m towards the downwind edge (Figure 8.6 and 8.7). The mean gas concentrations ranged between 0.002 mg m^{-3} to 0.45 mg m^{-3} for slurry surface spray and 0.002 mg m^{-3} to 0.18 mg m^{-3} for the injected application. The measured averaged NH_3 gas emission flux from trial 1 following surface spray and injection application are shown in Figure 8.8 and 8.9.

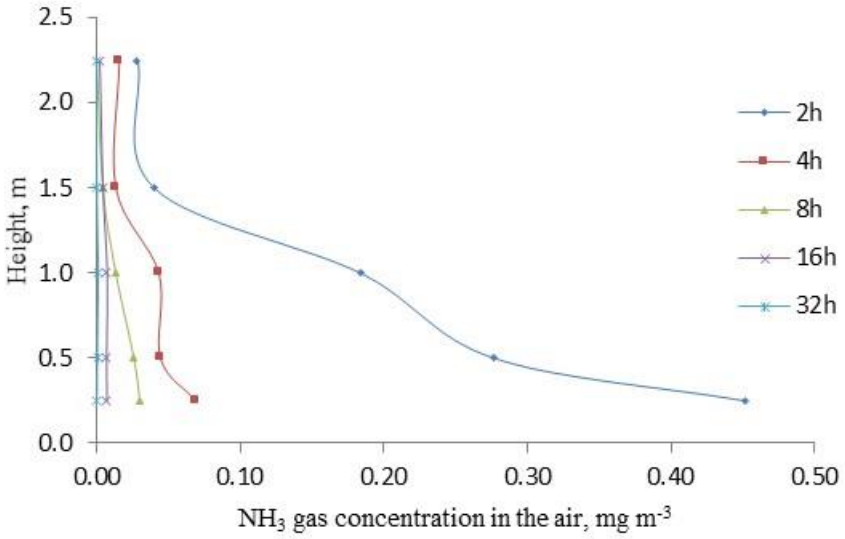


Figure 8. 6: NH_3 gas concentrations (gas profile) in the air measured at each height (downwind-upwind) for 2 - 32 hours following slurry application: Surface spray, Trial 1

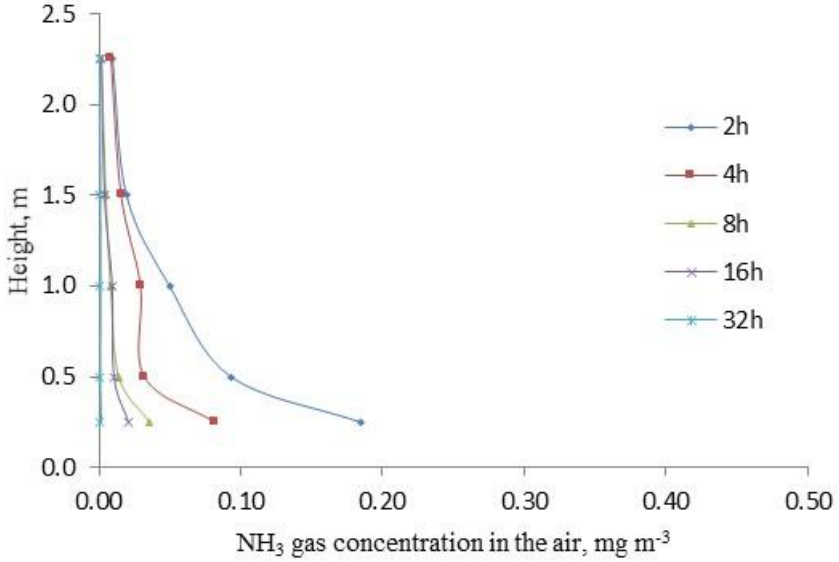


Figure 8. 7: NH_3 gas concentrations (gas profile) in the air measured at each height (downwind-upwind) for 2 - 32 h following slurry application: Injected application, Trial 1

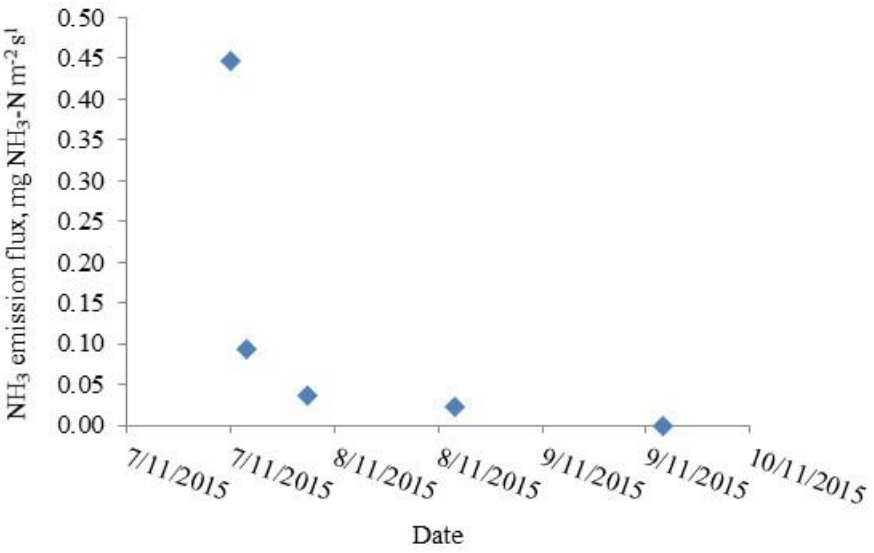


Figure 8. 8: Pattern of NH_3 gas loss [averaged flux (downwind-upwind)] following slurry application measured between 2 - 32 h of slurry application: Trial 1, Surface spray application at 10:00 AM

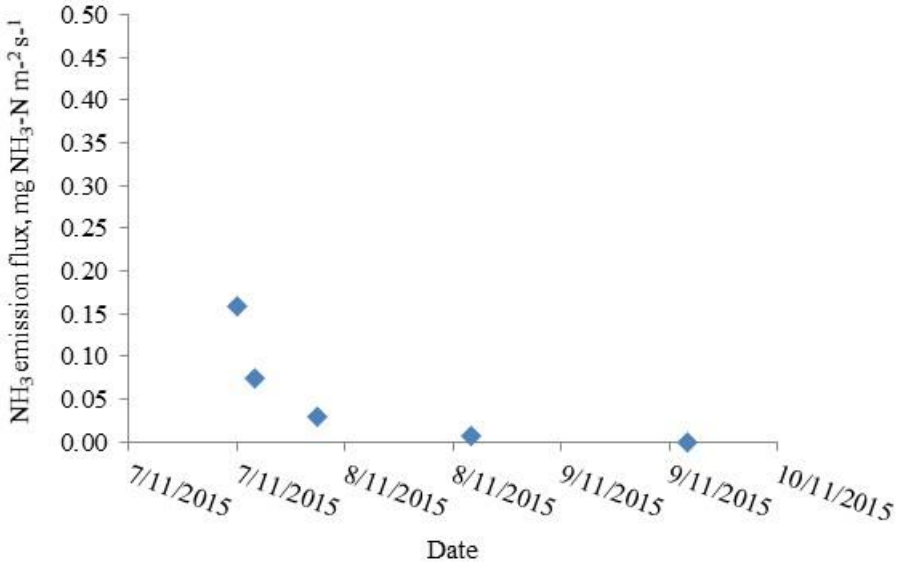


Figure 8. 9: Pattern of NH_3 gas loss [averaged flux (downwind-upwind)] following slurry application measured between 2 - 32 h of slurry application: Trial 1, Injected application at 10:00 AM

The flux data clearly showed that NH_3 emissions peaked soon after the application and declines over the passage of time. Notably wind speed and temperature, determinants of evaporation, drop in the afternoon and evening as well (Figure 8.4 and 8.5) but by the next day when wind speed and temperature peak around 14.00 h low concentrations of NH_3 were trapped leading to low flux rates. Changing the traps regularly allowed day and night measurements to be compared and also enabled to calculate the mean day and night

fluxes. The results from the acid traps showed that highest NH_3 flux rates 0.45 $mgm^{-2}s^{-1}$ for surface spray and 0.16 mg m^{-2} s^{-1} for slurry injection were recorded in the daytime shortly after application when the air temperature was high and flux rates dropped with drop in temperature at night (Table 8.3)

Table 8. 3: Mean day and night NH_3 emission flux following slurry surface spray and injection; Trial 1

Application technique	Mean day NH_3 flux mg NH_3-N m^{-2} s^{-1*}	Mean night NH_3 flux mg NH_3-N m^{-2} s^{-1*}
Spray	0.45	0.02
Injection	0.16	0.03

*mean of all gas concentrations measured at each height

8.3.3.1 Trial 2 Autumn: Meteorological data

For autumn application, the wind speed ranged between 0.04 m s^{-1} and 3.78 m s^{-1} and averaged at 1.24 m s^{-1} for the experimental period (Figure 8.10). Day time temperature peaked at 17.4 ºC and the night time low temperature was 7.3 ºC and average of 13.1 ºC for the trial period (Figure 8.11).

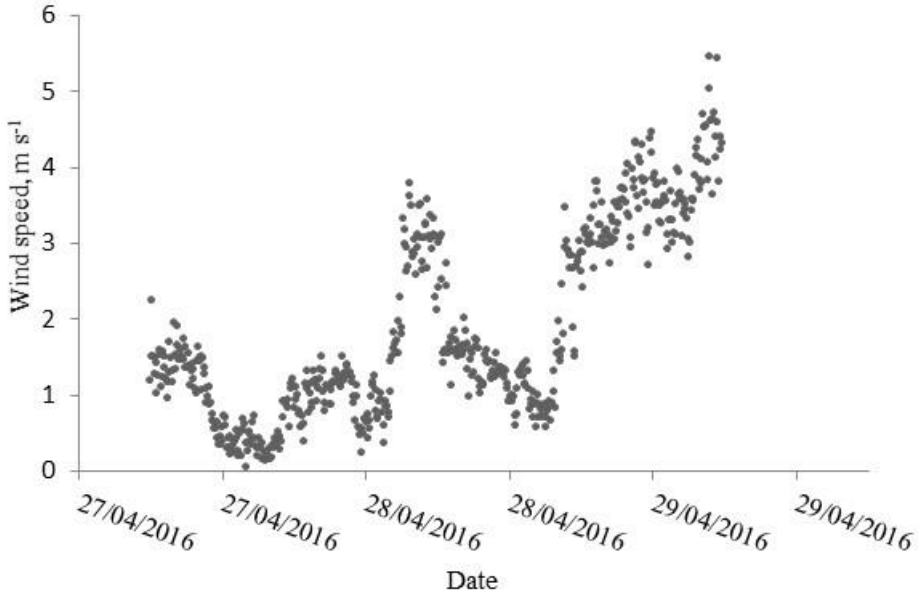


Figure 8. 10: Trend in wind speed (averaged every 5 minutes) over the experimental period: Autumn application, Trial 2

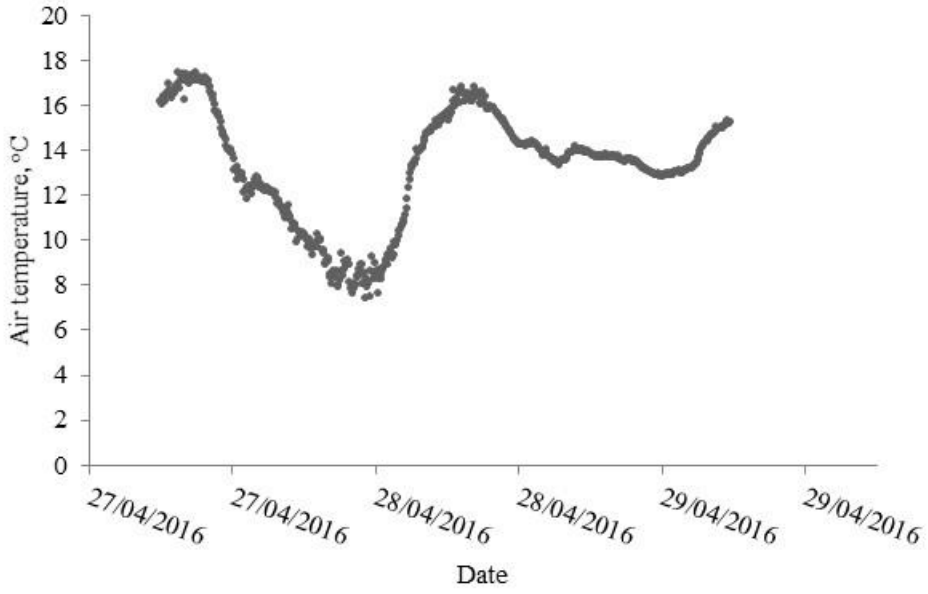


Figure 8. 11: Trend air temperature (averaged every 5 minutes) over the experimental period: Autumn application, Trial 2

8.3.3.2 Trial 2 Autumn: Measured ammonia gas concentrations

For autumn application, NH_3 gas profile in the air measured at each height (downwind-upwind) are shown in Figure 8.12 and 8.13 following slurry surface spray and injection. The gas concentrations measured at upwind edges of the paddocks were used to estimate the background concentrations of gas. The same trend of NH_3 gas profile in the air at each height was observed as in explained in section 8.3.2.2. The mean gas concentrations ranged between 0.002 mg m^{-3} to 2.27 mg m^{-3} for slurry surface spray and 0.002 to 0.59 mg m^{-3} for injected application measured at each height following slurry applications. The time averaged NH_3 gas emission flux from Trial 2 following spray application and injection application are reported in Figure 8.14 and 8.15.

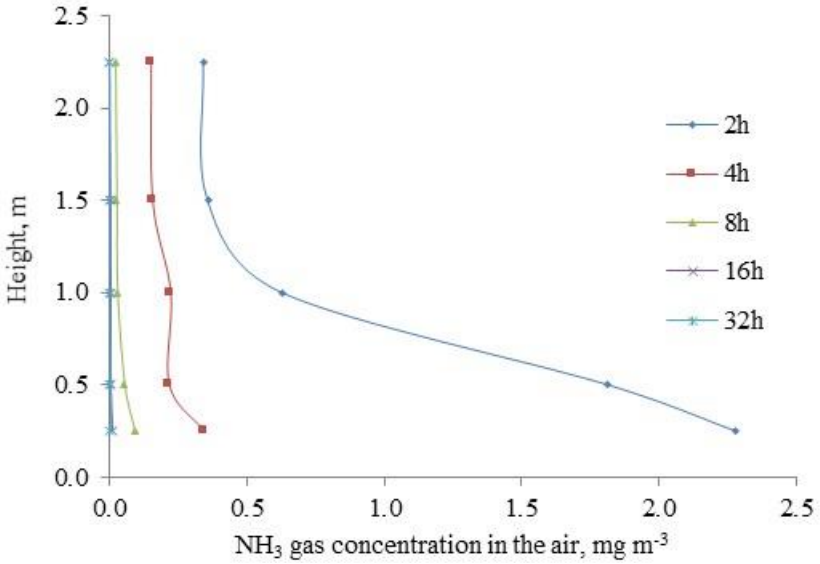


Figure 8. 12: NH_3 gas concentration (gas profile) in the air measured at each height (downwind-upwind) for 2- 32 h following slurry application: Surface spray; Trial 2

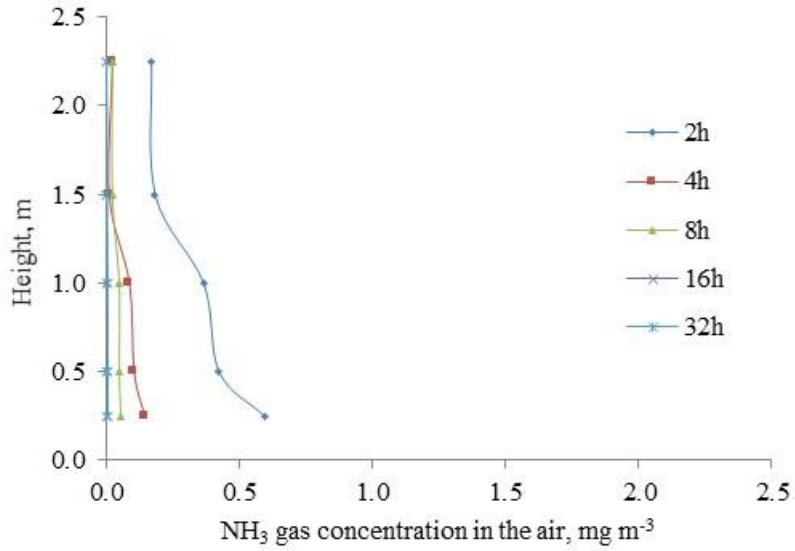


Figure 8. 13: NH_3 gas concentration (gas profile) in the air measured at each height (downwind-upwind) for 2- 32 h following slurry application: Injected application; Trial 2

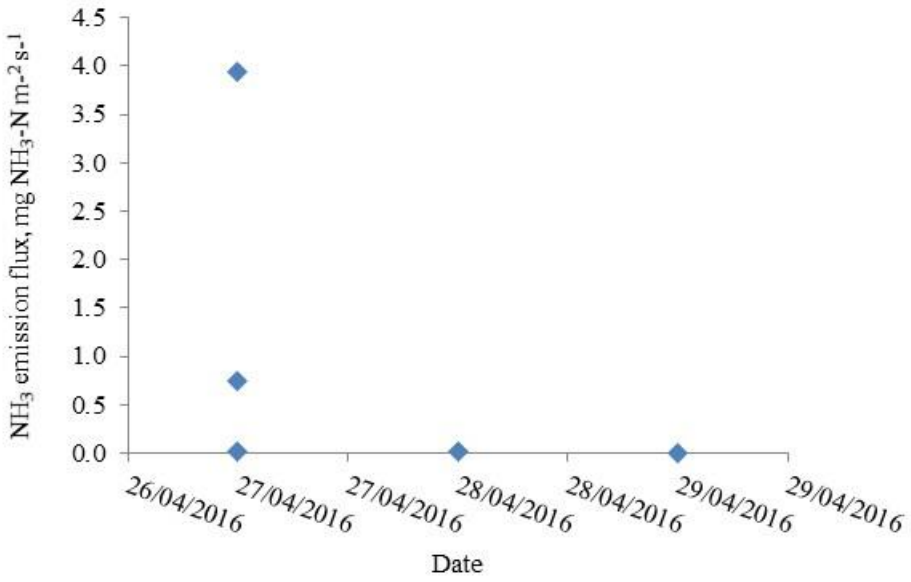


Figure 8. 14: Pattern of NH_3 gas loss [averaged flux (downwind-upwind)] following slurry application measured between 2 - 32 h of application: Trial 2, Surface spray application at 12:00

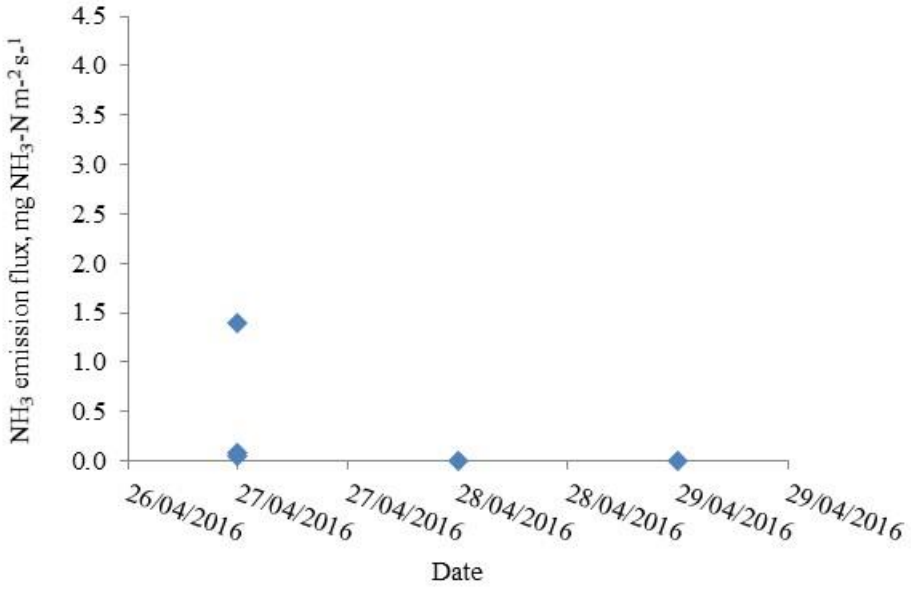


Figure 8. 15: Pattern of NH_3 gas loss [averaged flux (downwind-upwind)] following slurry application measured between 2 - 32 h of application: Trial 2, Injected application at 12:00

A similar trend in NH_3 emission flux following autumn slurry applications was found as observed in summer applications. The flux data again showed that NH_3 emissions peaked soon after the application and declines over the passage of time. Notably wind speed and temperature, determinants of evaporation, drop in the afternoon and evening as well (Figure 8.10 and 8.11) but by the next day when wind speed and temperature peak around

14.00 h and low concentrations of NH_3 were trapped leading to low flux rates. The results from the acid traps showed that highest NH_3 flux rates 3.93 mg m^{-2} s^{-1} for surface spray and 1.40 mg m^{-2} s^{-1} for slurry injection were recorded in the daytime shortly after application when the air temperature was high and flux rates dropped with drop in temperature at night (Table 8.4).

Table 8. 4: Mean day and night NH_3 emission flux following slurry surface spray and injection; Trial 2

Application technique	Mean day NH_3 flux mg NH_3-N m^{-2} s^{-1*}	Mean night NH_3 flux mg NH_3-N m^{-2} s^{-1*}
Spray	3.93	0.02
Injection	1.40	0.02

*mean of all concentrations measured at each height

8.3.4. Summary of Both Trials

8.3.4.1 Time after application

In both summer and autumn trials rates of NH_3 volatilization were calculated from the time averaged flux as described in Chapter 7. The emissions peaked between 0-4 hours of slurry application reaching background levels after 24 hours (Figures 8.8, 8.9, 8.15 and 8.16) that's why measurements were stopped after 48 hours. These results agree with findings of (Salazar et al. 2014; Webb et al. 2010) that most NH_3 is volatilized within 4 hours of slurry application to soils.

8.3.4.2 Slurry characteristics and N application rate

In this study N application rate was different for both trials. The N application rate for autumn application was 3 fold more than summer applications but the DM content at 0.6% was only slightly higher than the summer effluent at 0.4%. The slurries or FDE generated on NZ dairy farms are commonly very dilute because of mixing with cleaning water and rain, which is a characteristic of pasture based dairy grazing (Li et al. 2015). The FDE in NZ has been characterized to have 0 - 5% DM (Houlbrooke et al. 2011). In this study the DM content was only 0.4% and 0.6% which would give high infiltration rates under the soil moisture conditions that prevailed and would explain the lower volatilization rates of the land applied slurry. Despite the high N application rate for

autumn application there wasn't a remarkable difference in N losses which was partly because of lower daily ETR and soil available water in autumn over 32 hours (Table 8.5).

8.3.4.3 Summer vs Autumn weather and day length

The other main difference to rate of N application was time of application. For summer applications slurry was applied at 10 am in the morning and autumn application was applied at 12 pm noon. NH_3 air concentrations were higher for the autumn trial (Trial 2) immediately measured after the higher N application rate. This was particularly notable for the spray treatments. Although the NH_3 gas concentrations in the acid traps and flux rates were higher in autumn than the summer application wind speeds were lower immediately following the applications (c.f. Figure 8.8, 8.9, 8.15 and 8.16) contributing to similar NH_3 flux rates. One of the reasons for higher emission flux was the high TKN and TAN content of the slurry. Furthermore, there's was a slight difference in air temperature for both applications but timing and the longer summer days maintained a higher rate of NH_3 emissions as compared to autumn applications. These contrasting summer and autumn results support the fact that NH_3 emissions are positively related to air temperature and follow a diurnal pattern and were are consistent with previous researchers (Sommer et al. 1991; Misselbrook et al. 2005a). In Chile, (Martínez-Lagos et al. 2013) applied 100 kg N ha^{-1} dairy manure to grassland in spring and winter and quantified NH_3 emissions using micrometeorological techniques. They found 7 and 8% losses in winter compared to 16 and 21% losses in spring, the losses were attributed to environmental conditions particularly temperature. High air temperature, air speed and low humidity will accelerate the drying of manure which decreases volatilization (Huijsmans et al. 2003; Misselbrook and Powell 2005; Sommer and Hutchings 2001). Some studies have reported significant relationship between wind speed (lower than 2.5 m s^{-1}) and NH_3 emissions flux but emissions didn't increase when wind speed increased from 2.5 to 4 m s^{-1} (Sommer et al. 1991; Thompson et al. 1990). In current trials the average wind speed for summer and autumn application were 1.69 m s^{-1} and 1.88 m s^{-1}, respectively.

Weather conditions and manure characteristics are two important factors driving NH_3 emissions. Warm and sunny days and wind speed plays a key role in NH_3 volatilization. The magnitude of NH_3 emissions is driven by weather conditions in many ways for example high temperature, windy and sunny weather accelerates evapotranspiration. The

diffusion of NH_{3aq} from the higher concentrations on and in the soil is increased by the lower partial pressure of NH_3 in the atmosphere close to the ground directly above the applied slurry. NH_3 volatilization rate was found to be related to daily evapotranspiration rate (ETR), which is consistent with the findings of (Meisinger and Jokela 2000). ETR was higher after the summer application than the autumn application because summer ETR was not limited by topsoil available water content (Table 8.5). Higher NH_3 emissions with higher ETR is consistent with trend in NH_3 emissions from the storage pond when TAN concentration in slurry didn't change much (Chapter 7) and also consistent with the findings of (Dämmgen and Hutchings 2008; Ryden and Mcneill 1984; Sommer and Hutchings 2001). These researchers found a positive relationship between rate of NH_3 emission and evapotranspiration rate. The losses were low with reduced infiltration and ETR rates but increased with rainfall. The rate of surface ETR that provides the energy for gas exchange is highly dependent on temperature and solar radiation which accelerates the rate NH_3 volatilization (Meisinger and Jokela 2000). The low ET rate in second trial did not result in low emission flux because of the high TAN content of the slurry. This suggests that the elevation in TAN concentrations after agitating the pond ready for land application could become a dominant factor influencing NH_3 emissions.

Table 8. 5: Rate of daily evapotranspiration (mm) and NH_3 losses (kg N ha^{-1}) over 32 h from the land application of slurry

Date	Topsoil Root zone available water mm	Daily evapotranspiration rate (ETR) mm	Surface spray application loss over 32 h kg N ha^{-1}	Injected application loss over 32 h kg N ha^{-1}
7/11/2015	139.21	4.04		
8/11/2015	135.72	3.22		
9/11/2015	132.12	2.15	*1.5	*1.0
27/04/2016	77.93	1.20		
28/04/2016	76.73	0.93		
29/04/2016	75.37	0.93	*6.9	*2.8

*Single replicate treatments, statistical analysis not possible for comaprison

8.3.4.4 Spray vs Injection

Slurry incorporated in soil through injection brings manure deeper into soil and covers it with soil more comprehensively which reduces the rate of NH_3 volatilization. In this

experiment NH_3 volatilization rates from the surface spray and injection were 1.5 kg N ha[1] and 1 kg N ha^{-1} for the early summer application and 6.9 kg N ha^{-1} and 2.8 kg N ha^{-1} for the autumn application over 32 hours (Table 8.5). The % NH_3-N losses were 2% from slurry surface spray and 1.4% from slurry incorporation through injection for summer application and 3% from slurry surface spray and only 1% from injected application of slurry in autumn. This field trial aimed at quantifying and comparing NH_3 emissions from slurry reapplication to dairy grazed pastures through surface spray and injection which makes it unique to other studies conducted in NZ on FDE applications, which have mainly studied N loss mitigation though the use of nitrification or urease inhibitors and season of application. However, lack of treatment replicates statistical significance of the differences in emission between the surface spray and injection was not possible to provide scientifically sound comparison. The main mechanism for reducing NH_3 loss with injection is that injected slurry flows directly in the soil reducing the surface area for volatilization losses. When slurry is surface sprayed it has a larger surface area compared to slurry directly injected. The results presented in this Chapter clearly showed that emissions can also be mitigated by using a slurry injection application technique. These results are consistent with those reporting that incorporating slurry (injection) directly into the soil reduces the rate of volatilization (Rodhe and Etana 2005). There's an ample literature on slurry injection technique reducing NH_3 emission loss by 40 to 90% compared to surface applications (Huijsmans et al. 2003; Ndegwa et al. 2008; Webb et al. 2010; Holly et al. 2017).

Furthermore, a low emission rate from slurry injection compared to surface spray is important when considering how to reduce NH_3 loss from effluents with high DM content. In a NZ study (Li et al. 2014) studying the impact of liquid and semi-solid FDE amended with urease inhibitors applied to pastures over different seasons (spring, summer and autumn) on NH_3 emissions. They found that NH_3 emissions ranged from 0.6 % - 19 % of applied N (application rate 100 kg N ha^{-1}) from fresh and stored manures and emissions in summer were higher than spring and autumn applications. The authors found that dry matter (DM) content of slurry is an important factor promoting NH_3 emissions because the slurry with high DM doesn't infiltrate through the soil and remains on the soil surface. Injection of storage pond sludge is likely to overcome the high emissions associated with effluent of high DM content.

8.4 Conclusions

The two small field trials carried over early summer and early autumn provides a brief case study of the factors influencing NH_3 emissions from the land application of freestall barn, holding pond slurry. Ammonia losses are very small (1 - 3%) from the final stage of manure management.. The risk for NH_3 losses appears higher when slurry is spread in the summer compared to when spread in cooler seasons because of warmer weather and longer days and high evaporation rates in summer. The results of this experimental work indicate that incorporating slurry into the soil through injection may be more efficient for reducing NH_3 emissions as compared to surface spray. There was no remarkable difference in %N losses from both techniques from this single replicate study. Future experiments with replicate treatments and conducted over longer time period and uniform application rates can provide more insights on magnitude of emissions from different application techniques.

Chapter 9

Summary, Conclusions and recommendations for future work

9.1 Introduction

This research aimed at developing and standardising low cost and effective techniques suitable for quantifying NH_3 gas emission losses from various stages of manure management. The lack of NZ data from a duration controlled dairy grazing housing system mainly due to unavailability of suitable techniques. The factors affecting NH_3 emissions from various stages are well documented but less is known about the slurry characteristics and environmental factors influencing NH_3 emissions from duration control grazing system practiced in Manawatu region of NZ. Laboratory and field experiments were conducted to study the effect of slurry characteristics and environmental factors on magnitude of NH_3 emissions from all the stages

9.1.1. Development of appropriate techniques for quantifying ammonia losses from subsequent stages of manure management

The objective of this chapter was to develop suitable and convenient techniques for measuring and estimating NH_3 losses from all the subsequent stages of manure management. In NZ a few studies measuring NH_3 gas emissions from urine and effluent application to dairy grazed pastures have used dynamic chambers with active acid traps and micrometeorological techniques. These techniques involve significant investment in equipment so an alternative technique of placing the NH_3 source in 1L preserving jars with passive acid traps. For evaluation of total emissions from cow barn slurry over a collection period of 60 h jars were 80 and 98% as efficient as dynamic chambers. However for measuring rates of NH_3 emissions for shorter periods (0 - 24 h) the passive traps collected 8%, 10%, 27% and 61 - 73% after 4, 8 and 32 h of that collected by the dynamic chambers. The preserving jar, passive trap technique enabled the relative emission loss of NH_3 from urine and dung samples reported in chapter 4, 5 and 6 and provided an overview of the factors (e.g. cow diet, slurry age and depth) driving NH_3 emissions from the freestall barn's laneways and slurry channel.. For measuring NH_3 emissions from outdoor surfaces a simple mast carrying active and passive acid traps and

a sonic anemometer were evaluated as a method of measuring NH_3 concentrations in the air and wind speeds such that integrated horizontal NH_3 flux (IHF) calculations could be completed. These techniques were then deployed for measuring NH_3 losses from the effluent storage pond Chapter 7 and from slurry applications to the field (Chapter 8).

9.1.2. Influence of the urinary urea N on ammonia emission flux from urine dung mixtures

The research objective of Chapter 4 was to develop a simple model to predict NH_3 losses from the deposition of urine and dung that form slurry mixtures in freestall barn laneways. Feeding different levels of dietary crude protein to dairy cows generated various concentrations of urea N (~700 to 5500 mg N L^{-1}) in urine. As urea concentrations in urine increased, the pH and NH_3 losses from urine-dung slurries increased. An empirical models based on initial urea concentration and current pH was able to explain 80% of the variation in NH_3 emissions from ageing (0 - 144 h) urine dung mixtures.

9.1.3: The influence of dietary crude protein intake by cows on ammonia emissions from urine-dung, slurry mixtures.

The level dietary crude protein intake by dairy cows strongly influences the amount of N excreted in urine because cows only retains 5 - 10% while rest is excreted as urea N in urine. The main objective of Chapter 5 was to investigate the impact of various dietary crude protein intake levels (13.5 - 25%) on NH_3 emissions and how these compare to urine deposition on grazed pastures under laboratory conditions. The results clearly showed that reducing the % CP content of a cow's diet can reduce NH_3 emissions by upto 25%. This could be an effective management strategy for reducing overall losses from cows housed in freestall barns but is also likely to reduce losses from collecting areas, feed pads and storage ponds.

9.1.4: Ammonia emissions from a naturally ventilated dairy cow barn

The use of wintering barns is relatively new to various dairy cows grazing systems practiced in NZ. It's unknown how the introduction of high supplement feed, various management practices like scraping schedule, storage of slurry in underneath storage

channels and slurry chemical characteristics will influence NH_3 emissions. One use of wintering barns is to hold and feed cows overnight (~16 h) during periods of inclement weather. The research objective of Chapter 6 was to estimate the NH_3 loss from an overnight housing of 200 cows in the Massey University freestall barn. Two methods were tested. In the first, laneway slurry and channel slurry samples were collected and the NH_3 emissions per unit surface area measured in an ex-situ experiment using passive NH_3 trapping in preserving jars. Secondly, these emissions were compared to the in-situ measurement of NH_3 concentrations and barn opening ventilation rates using active acid scrubbers coupled with 3D sonic anemometer to measure NH_3 losses from various openings of the barn. The in-situ method estimated losses of 2 - 3 kg NH_3 from the barn in 16 h. The uncorrected ex-situ measurement estimated losses of 0.9 kg NH_3 in 16 h, but when corrected for the low % of recovery by passive traps in 16h the values ranged between 2.1 - 2.6 kg NH_3-N loss for 16 hours. In a freestall barn, lane scrapers could operate more frequently to reduce areas of slurry. For example if scrapers operated every 2, 4, 8 or 16 h removing slurry to the channel for cows held in the barn overnight (16 h) the slurry volume exposed to NH_3 loss would be reduced but if the scraper lane surfaces remain wet and are re-covered quickly by more urine and dung deposition then the surface area for NH_3 loss remains the same. Therefore the effect of frequency of lane cleaning by scraper on NH_3 reduction is uncertain and would have to be measured in relation to dung and urine deposition rates.

9.1.5: Ammonia emissions from slurry storage pond

Long-term NH_3 gas emissions from storage pond were monitored using improved IHF methodology over winters. The slurry is stored from 30 to 90 days before its strategic reapplication to land; therefore it's very important to know the characteristics both environmental and slurry regulating NH_3 gas emissions from the pond. The study aimed at studying the trend in slurry nutrient concentration (TAN, TKN, and TKP), pH and NH_3 emission flux from the surface of static slurry storage pond. Among various factors slurry pH and daily evapotranspiration rate were found to the dominant factors driving emissions. A model based on daily evaporation rate (mm day^{-1}) explained 81% of the variation in NH_3 emissions from the pond measured over two periods of varying weather conditions. Based on the trend in pH and the daily ET a model was developed to predict and report gas emissions from the pond over an extended period of time 30, 60 and 90

days. The major conclusion is that % losses increase linearly with increased storage time and will accelerate during warm summer months. Regular reapplication to land will reduce pond surface area and NH_3 loss. Pond covers should be investigated as emissions during storage are the largest.

9.1.6: Slurry reapplication to land

There is an immense literature on NH_3 emissions from urine deposition on dairy grazed pastures and soils receiving farm dairy effluents in NZ and on factors controlling the magnitude of emissions. However, it's not known how various slurry application techniques are going to influence the magnitude of emissions following re-application of slurry collected from a storage pond receiving slurry from housed cows. The objective of this study was to quantify and compare losses from two different application techniques (slurry spray vs injection) and to report the %N losses from the final stage of manure management chain. Measurements made using the integrated horizontal flux technique indicated that NH_3 volatilisation losses for 32 h after spreading were small 1.4% – 2% in summer and 1% - 3% (injection vs spray) in autumn of the TKN applied.

9.2 An estimate of ammonia loss from various stages of manure management after housing cows.

On completion of NH_3 loss measurements at all stages of manure management it was possible to construct a partial NH_3 loss budget to illustrate the relative NH_3 losses associated with the temporary housing of cows in a freestall barn.

A case study was built around 200 cows being housed for 16 h d^{-1} for 30 days at the beginning of the 2016 lactation season (15th July). It was assumed cows were excreting 250 g N cow^{-1} day^{-1} as dung and urine and when confined for 16 h and the TKN of the slurry is 4300 g m^{-3}, then approximately 7.7 m^3 of slurry containing 33 kg TKN is produced in 16 h. The generation of slurry N is illustrated in Figure 9.1. In Chapter 6 it was estimated that an average of 2.8 kg NH_3-N loss occurred from the barn when housing for 16 hours. The accumulated N loss from the barn is 85 kg NH_3 –N (Figure 9.1) or 8.5% of the N excreted as dung and urine. Accumulated N loss from the effluent stored in the pond for 30 days was calculated using the model developed in Chapter 7 and the climate data for the 30 day period 15th July to 13th Aug 2016. Losses from the pond during those

30 days amounted to 12.7% of the N excreted as dung and urine. Reapplication of slurry accumulated in 30 days (325 m^3) to land by injection would cause an NH_3 loss of ~3.9 kg NH_3-N (Figure 9.1). This simple analysis illustrates that the largest loss of NH_3 occurs during the storage of effluent in an open pond. Future research to mitigate NH_3 losses created by housing cows should focus on the reduction of NH_3 loss from ponds. Obviously pond covers that reduced ET and or allowed NH_3 trapping would create large reductions in NH_3 losses occurring from housed cows. Future work including long term measurements covering different seasons is highly recommended for developing accurate NH_3 emissions factors for off-paddock dairy facilities used in NZ.

It is important to state that we cannot estimate emission factors from this research, long term measurements covering different seasons is highly recommended for developing emissions factors from off-paddock dairy facilities used in NZ.

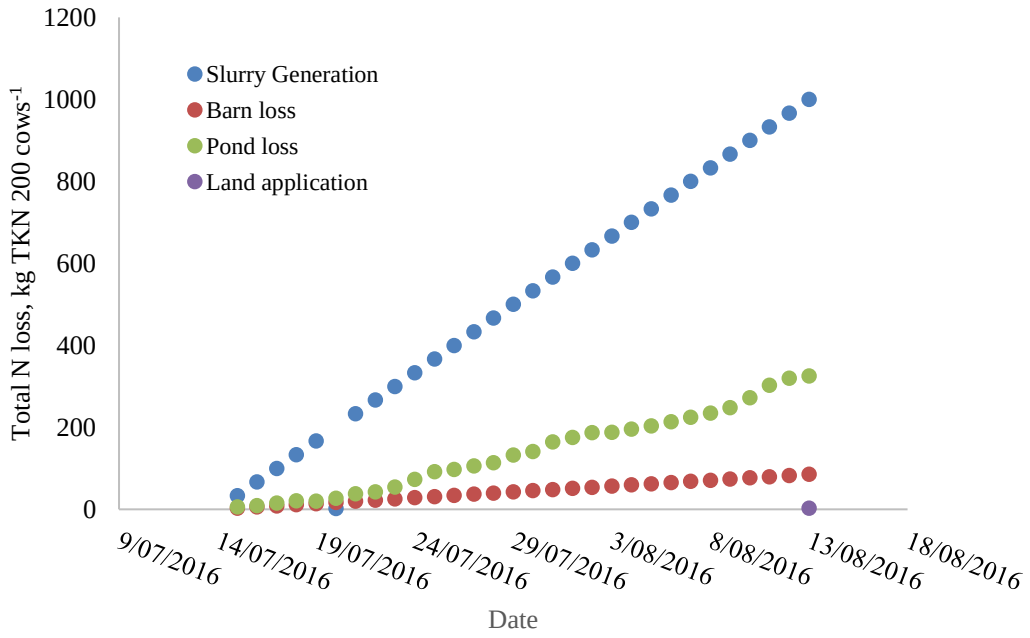


Figure 9. 1: Accumulated slurry generated by housed cows followed by NH_3 loss (kg N 200 $cows^{-1}$) from the barn, storage pond and slurry re-application to land.

9.4 Future recommendations

The main puropose of this research is to contribute to the knowledge (management and climatic factors) on NH_3 gas emissions from a hybrid dairy grazing-housing system. Based on the conclusions drawn from all experimental chapters and to fully comprehend these conclusions more research is needed. This research highlighted many important

questions for example, results of chapter 4 and 5 indicate that dietary changes may reduce NH_3 emissions from combined urine dung slurries by 25% but how these changes are going to impact indirect N_2O emissions is still not known. The cows are housed during winters and deposited excreta is stored over the same time period, the N losses during winters from storage pond are low because of low ET rates but indirect N_2O emissions from the urine patches may be high because the soils are wet. Therefore, should future projects should focus at comparative seasonal losses of NH_3 and N_2O from all pasture farms (i.e. N_2O losses from dung and urine deposited in the paddock) at the same time that excreta is being stored in ponds for housed cows. i.e. cows are housed in winter. Long term experiments under various barn/climatic conditions will be useful in providing insights on the effect of indoor climatic conditions and management practices on NH_3 gas emissions. Long term measurements of ventilation rate will add credibility to indirect estimation of ventilation rate using 3D sonic anemometer. Furthermore, rainfall, wind speed, manure pH, soil pH, soil chemical and physical properties along with manure chemical characteristics should be samples/measured at the same time and periodically to monitor the amount of total N in the soil and in the manure over time for land application trails. Better understanding of these factors will help understand trend in NH_3 volatility and these factors could be used to predict NH_3 emissions from various stages of the manure management chain.

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